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XVII.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part IV. Chain Compounds of Sulphur* (continued).

By Prafulla Chandra Rây and Prafulla Chandra Guha.

ı this investigation, the reactions of several actual and potential ercaptans, some of them cyclic, have been studied. It was ex-
ɤted that in these, the molecules being of a more complex nature, ıe radicle, especially $\cdot SHgNO_2$, would far more readily part comıny with the parent substance and lead an independent existence ı the compound, $3(SHgNO_2),HgO$ (T., 1917, **111**, 101). The ·sult has proved to be just the reverse.

5-Thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole,

$$\begin{matrix} NPh\cdot N \\ | \\ CS—S \end{matrix}\!\!>C\cdot SH,$$

elds, with mercuric nitrite, the corresponding mercaptide nitrite ompare T., 1916, **109**, 131),

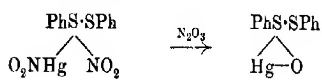
$$RSH + Hg(NO_2)_2 = RS\cdot HgNO_2 + HNO_2.$$

ercuric nitrite and phenyl mercaptan furnish a compound, h_2S_3Hg, evidently a mercaptide, and sometimes another oxy-salt, $PhS,HgO)_2$. It is only in exceptional cases (see p. 264) that ıe expected mercaptide nitrite, $PhS\cdot HgNO_2$, is obtained, and then ıly in an impure form.

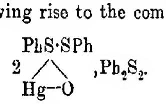
The reaction appears to proceed in the following stages:

$$PhSH + Hg(NO_2)_2 = PhS\cdot HgNO_2 + HNO_2.$$

ıe nitrous acid thus liberated oxidises another pair of molecules phenyl mercaptan to diphenyl disulphide, and the latter then rms with mercuric nitrite the compound,



ʼo molecules of this compound combine with a molecule of ıhenyl disulphide, giving rise to the compound,



3-Phenyl-5-methyl-2-thiohydantoin gives the mercaptide nitrite,

$$\begin{matrix} CO—NPh \\ | \\ CHMe\cdot N \end{matrix}\!\!>C\cdot SHgNO_2.$$

Potential Mercaptans.

The interaction of mercuric nitrite and the aryl substitute thiocarbamides, thiosemicarbazides, thiocarbazides, etc., follows th ordinary course, but no detachment of the organic radicle take place. Thus with phenylthiocarbamide we have

$$NHPh{\cdot}C(NH_2){:}S \xrightarrow{Hg(NO_2)_2} NHPh{\cdot}C({:}NH){\cdot}S{\cdot}HgNO_2 \longrightarrow$$
$$NHPh{\cdot}C({:}NH){\cdot}S(HgNO_2){<}^{Hg}_{O}.$$

Attention may also here be directed to the interesting analogou case of potassium phenyldithiocarbazinate, which combines in itsel the function of a real and of a potential mercaptan, thus:

$$NHPh{\cdot}NH{\cdot}CS_2K \xrightarrow{Hg(NO_2)_2} NHPh{\cdot}N{:}C(SH){\cdot}SK \longrightarrow$$
$$NHPh{\cdot}N{:}C(S{\cdot}HgNO_2){\cdot}S(HgNO_2){<}^{Hg}_{O}$$

The sulphur atom belonging to the potential mercaptan alo becomes quadrivalent.

Migration of Alkyl Radicles.

When thiocarbanilide methyl ether is treated with mercur nitrite, the methyl group migrates to the neighbouring nitroge atom, hydrogen taking its place, thus:

$$NHPh{\cdot}C({:}NPh){\cdot}SMe \xrightarrow{Hg(NO_2)_2} NMePh{\cdot}C({:}NPh){\cdot}SH \longrightarrow$$
$$NMePh{\cdot}C({:}NPh){\cdot}S{\cdot}HgNO_2$$

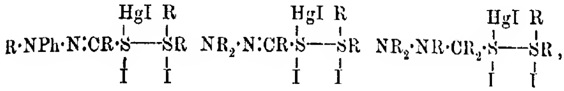
That the reactions described above are of wide application i borne out by the behaviour of 5-methylthiol-2-thio-3-phenyl-2:3 dihydro-1:3:4-thiodiazole, which with mercuric nitrite gives th compound,

$$\begin{array}{l} NPh{\cdot}NMe \\ | \\ CS\text{——}S \end{array}{>}C(HgNO_2){\cdot}S{\cdot}HgNO_2.$$

Reaction with the Alkyl Iodides: Formation of Mono-, Di-, and Tri-sulphonium Compounds.

The reaction follows the general course with this material differ ence, that the complex radicle, being overweighted, can no longe retain its entity, but the less stable part of it is usually rupture Of special significance from this point of view is the rupture o the ring of the heterocyclic mercaptide nitrites. When th mercaptide nitrite of 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4

thiodiazole is digested with an alkyl iodide, the product (I) is obtained, and by further action of the alkyl iodide, the phenyl

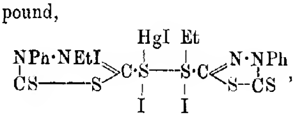


(I.) (II.) (III.)

group is displaced by the alkyl group and the compound (II) is formed. Finally, two more alkyl groups are attached, with the production of the compound (III).

By the action of methyl iodide, two compounds corresponding with stages (I) and (III) have been isolated, whereas in the case of ethyl iodide only one compound has been obtained, which corresponds with stage (II).

When 2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole disulphide dissolved in carbon disulphide was heated under reflux with ethyl and mercuric iodides, not only was there no rupture of the thiodiazole rings, but one of the tertiary nitrogen atoms became quaternary by combining with a molecule of ethyl iodide, and the following compound,



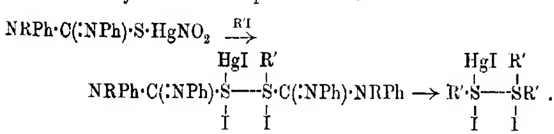
was obtained.

The action of alkyl iodides on phenyl mercaptide nitrite follows the usual course and yields compounds of the general formula $PhRS_2,HgI_2,RI$.

An interesting monosulphonium compound has been obtained from the mercaptide nitrite of thiocarbanilide. The reaction probably takes place as shown below:

$$NHPh\cdot C(:NPh)\cdot S(HgNO_2)<\begin{matrix}Hg\\ |\\ O\end{matrix} \xrightarrow{EtI} CEt_2I\cdot SEtI\cdot HgI.$$

The interaction of mercaptide nitrites of thiocarbanilide alkyl ethers and alkyl iodide takes place as follows:



Experimental.

Interaction of the Potassium Salt of 5-Thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole and Mercuric Nitrite: Formation of the corresponding Mercaptide Nitrite,

$$\begin{array}{l} NPh\cdot N \\ \mid \\ CS\text{--}S \end{array}\!\!>C\cdot SHgNO_2.$$

The mercury salt was obtained sometimes anhydrous, but often combined with three, five, or eight molecules of water, the degree of hydration evidently depending on the dilution of the reacting substances. They all evolved nitrous fumes when treated with hydrochloric acid:

0·2724 gave 0·1187 Hg. Hg=43·59.

0·1100 „ 0·0810 CO_2 and 0·0187 H_2O. C=20·08; H=1·89.

0·1420 „ 10·2 c.c. N_2 at 25° and 760 mm. N=8·10.

$C_8H_5O_2N_3S_3Hg$ requires Hg=42·46; C=20·38; H=1·06; N=8·92 per cent.

The above with $3H_2O$:

Found: Hg=38·05; C=18·28; H=3·29; N=8·30; S=18·56.

Calc.: Hg=38·09; C=18·29; H=2·1; N=8·00; S=18·29 per cent.

The compound with $5H_2O$:

Found: Hg=35·75; C=16·92; H=3·20.

Calc.: Hg=35·65; C=17·12; H=2·67 per cent.

The compound with $8H_2O$:

Found: Hg=32·10; C=15·10; H=3·56; N=6·16; S=15·08.

Calc.: Hg=32·52; C=15·63; H=3·41; N=6·83; S=15·61 per cent.

Mercuric Nitrite and Phenyl Mercaptan.

Three different compounds have been isolated in this case. When an alcoholic solution of phenyl mercaptan is added slowly to an excess of mercuric nitrite solution, the reaction takes the ordinary course, and the mercaptide nitrite, $PhS\cdot HgNO_2$, is mainly formed. It is a dull yellow, light granular powder, and is a true nitrite. When, however, the mercaptan is rapidly added in excess, the whole of the mixture assumes a dirty yellow colour and nitrous fumes are evolved. On keeping, a white, granular powder is obtained which, when crystallised from hot benzene until quite pure, melts sharply at 146°. Under slightly varying conditions, an oxy-compound, $(3PhS,HgO)_2$, is formed. As is evident, it is not easy to control the reaction so as to give one product to the ex-

clusion of the others. The mercaptide nitrite is always found to be admixed with the other products of this reaction.

The mercaptide nitrite gave different results of analysis on different occasions, depending on the proportion of the compound, Ph_2S_3Hg, admixed with it; generally, however, the values were found to be intermediate between those required for the pure material and the compound, Ph_2S_3Hg.

The compound, Ph_2S_3Hg, melting at 146°, gave the following results:

0·1942 gave 0·0864 Hg and 0·3134 $BaSO_4$. Hg = 44·48; S = 22·16.

0·0964 gave 0·116 CO_2 and 0·0230 H_2O. C = 32·17; H = 2·7.

$C_{12}H_{10}S_3Hg$ requires Hg = 44·44; S = 21·30; C = 32·00; H = 2·30 per cent.

The compound, $(3PhS,HgO)_2$, gave the following results:

0·4016 gave 0·1506 Hg. Hg = 37·50.

0·4333 „ 0·5620 $BaSO_4$. S = 17·82.

0·1230 „ 0·1886 CO_2. C = 41·81.

$C_{36}H_{30}O_2S_6Hg_2$ requires Hg = 38·02; S = 18·25; C = 41·07 per cent.

The above two compounds were proved to be non-nitrogenous by combustion analysis.

Mercuric Nitrite and 3-Phenyl-5-methyl-2-thiohydantoin: Formation of the Compound, $\begin{matrix}CO{-}NPh\\ |\\ CHMe{\cdot}N\end{matrix}{>}C{\cdot}S{\cdot}HgNO_2,2H_2O$.

The compound was greenish-grey:

0·1981 gave 0·0954 HgS and 0·1110 $BaSO_4$. Hg = 41·51; S = 7·69.

0·1774 gave 0·1586 CO_2 and 0·0582 H_2O. C = 24·38; H = 3·65.

0·2836 „ 20·8 c.c. N_2 at 30° and 760 mm. N = 8·10.

$C_{10}H_{13}O_5N_3SHg$ requires Hg = 41·07; S = 6·57; C = 24·64; H = 2·67; N = 8·63 per cent.

Potential Mercaptans.

Mercuric Nitrite and Phenylthiocarbamide: Formation of the Compound, $NHPh{\cdot}C(:NH){\cdot}S(HgNO_2){<}\begin{matrix}Hg\\ |\\ O\end{matrix}$.

This was deep yellow:

0·3512 gave 0·2350 Hg and 0·1227 $BaSO_4$. Hg = 66·9; S = 4·8.

0·2015 „ 11·4 c.c. N_2 at 26° and 760 mm. N = 6·40.

$C_7H_7O_3N_3SHg_2$ requires Hg = 65·25; S = 5·22; N = 6·85 per cent.

Mercuric Nitrite and s-Diphenylthiocarbamide: Formation of the Compound, $NHPh\cdot C(:NPh)\cdot S(HgNO_2){<}\overset{Hg}{\underset{O}{|}}$.

This was a brownish-yellow, granular powder:

0·3422 gave 0·1970 Hg and 0·1069 $BaSO_4$. Hg = 57·57; S = 4·64.
0·3970 ,, 0·1141 CO_2 and 0·0244 H_2O. C = 22·27; H = 1·94.
$C_{13}H_{11}O_3N_3SHg_2$ requires Hg = 58·07; S = 4·64; C = 22·64; H = 1·60 per cent.

The above compound is only rarely formed. The product generally obtained conforms to the formula

$$Hg[NPh\cdot C(:NPh)\cdot S\cdot HgNO_2]_2:$$

0·1555 gave 0·0947 HgS and 0·0741 $BaSO_4$. Hg = 52·51; S = 6·55.
0·2275 gave 0·1367 HgS and 0·0992 $BaSO_4$. Hg = 51·80; S = 5·99.
$C_{26}H_{20}O_4N_6S_2Hg_3$ requires Hg = 52·43; S = 5·59 per cent.

Mercuric Nitrite and Thiosemicarbazide: Formation of the Compound, $Hg[N(NH_2)\cdot C(:NH)\cdot S\cdot HgNO_2]_2$.

An aqueous solution of the thio-compound was used. The product was a dull yellow, granular powder:

0·2715 gave 0·1870 HgS and 0·1362 $BaSO_4$. Hg = 68·87; S = 6·89.
0·1032 gave 11·8 c.c. N_2 at 32° and 760 mm. N = 12·60.
$C_2H_6O_4N_8S_2Hg_3$ requires Hg = 68·96; S = 7·36; N = 12·87 per cent.

Mercuric Nitrite and Diphenylthiosemicarbazide: Formation of the Compound, $Hg[N(NHPh)\cdot C(:NPh)\cdot S\cdot HgNO_2]_2$.

This is an orange-yellow, granular powder:

0·1797 gave 0·0925 Hg. Hg = 51·48.
0·2577 ,, 0·2498 CO_2 and 0·0523 H_2O. C = 26·21; H = 2·25.
0·1380 ,, 11·7 c.c. N_2 at 32° and 760 mm. N = 9·38.
$C_{26}H_{22}O_4N_8S_2Hg_3$ requires Hg = 51·11; C = 28·57; H = 1·87; N = 9·54 per cent.

Mercuric Nitrite and Diphenylthiocarbazide: Formation of the Compound, $Hg[N(NHPh)\cdot C(:N\cdot NHPh)\cdot S\cdot HgNO_2]_2$.

This is a pink, granular powder:

0·1667 gave 0·0965 HgS and 0·0607 $BaSO_4$. Hg=49·91; S=5·00.

0·1463 gave 0·1404 CO_2 and 0·0327 H_2O. C=26·14; H=2·48.

0·1167 ,, 11·7 c.c. N_2 at 30° and 760 mm. N=11·26.

$C_{26}H_{24}O_4N_{10}S_2Hg_3$ requires Hg=49·83; S=5·31; C=25·91; H=1·82; N=11·62 per cent.

Mercuric Nitrite and Phenylhydrazine Phenyldithiocarbazinate: Formation of the Compound,

$$NHPh\cdot N:C(SHgNO_2)\cdot S(HgNO_2)<\begin{matrix}Hg\\|\\O\end{matrix}.$$

This is a blackish-violet, granular powder:

0·1971 gave 0·1549 HgS and 0·1031 $BaSO_4$. Hg=67·71; S=7·18.

0·1651 gave 8·5 c.c. N_2 at 27° and 760 mm. N=5·89.

$_7H_6O_5N_4S_2Hg_3$ requires Hg=67·40; S=7·19; N=6·30; C=9·44 per cent.

The same compound is formed by the interaction of mercuric itrite and potassium phenyldithiocarbazinate. (Found: Hg=7·97; C=9·24; H=0·98; N=5·88 per cent.)

Mercuric Nitrite and Thiocarbanilide Methyl Ether: Formation of the Compound, $NMePh\cdot C(:NPh)\cdot S\cdot HgNO_2$.

This is an orange-yellow, granular powder:

0·2801 gave 0·1038 Hg. Hg=39·86.

0·2377 ,, 0·3027 CO_2 and 0·0738 H_2O. C=34·70; H=3·45.

0·2863 ,, 22·6 c.c. N_2 at 29° and 760 mm. N=8·99.

$C_{14}H_{13}O_2N_3SHg$ requires Hg=40·90; C=34·50; H=2·67; N=8·86 per cent.

Mercuric Nitrite and Thiocarbanilide Ethyl Ether: Formation of the Compound, $NEtPh\cdot C(:NPh)\cdot S\cdot HgNO_2$.

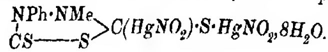
The substance is an orange-yellow, granular powder:

0·3730 gave 0·1478 Hg and 0·1874 $BaSO_4$. Hg=39·63; S=6·91.

0·1232 ,, 9·4 c.c. N_2 at 32° and 760 mm. N=8·43.

$C_{15}H_{15}O_2N_3SHg$ requires Hg=39·92; S=6·39; N=8·38 per cent.

Mercuric Nitrite and 5-Methylthiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole: Formation of the Compound,



A clear solution of the thio-compound in chloroform was vigorously agitated with mercuric nitrite solution for nearly half an hour, when an emulsion was formed which, after being allowed to remain overnight, gave a cream-coloured, granular mass:

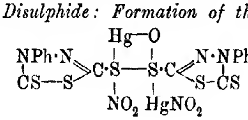
0·1984 gave 0·1055 HgS and 0·1384 $BaSO_4$. Hg=45·85; S=9·58.

0·1879 gave 0·0884 CO_2 and 0·0296 H_2O. C=12·83; H=1·75.

0·1603 ,, 10·2 c.c. N_2 at 30° and 760 mm. N=7·03.

$C_9H_{24}O_{12}N_4S_3Hg_2$ requires Hg=45·67; S=10·96; C=12·33; H=0·91; N=6·39 per cent.

Mercuric Nitrite and 2-Thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole Disulphide: Formation of the Compound,



(compare T., 1916, **109**, 133):

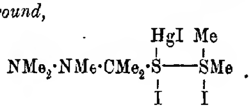
0·2940 gave 0·1288 Hg. Hg=43·80.

0·1190 ,, 9·00 c.c. N_2 at 30° and 760 mm. N=8·35.

$C_{16}H_{10}O_5N_6S_6Hg_2$ requires Hg=41·75; N=8·77 per cent.

Reaction with the Alkyl Iodides.

Interaction of the Mercaptide Nitrite of 5-Thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole and Methyl Iodide: Formation of the Compound,



The method of procedure is exactly the same as in the interaction of simple mercury mercaptide nitrites and the alkyl iodides. After heating with methyl iodide under reflux, a portion was left undissolved, which, when purified by washing several times with acetone, melted sharply at 127°. The portion soluble in acetone was purified by precipitation with ether, and melted at 107°:

0·3129 gave 0·0811 Hg. Hg=25·92.
0·4107 „ 0·1066 Hg and 0·3718 AgI. Hg=25·96; I=48·72.
0·0844 „ 0·0363 CO_2 and 0·0237 H_2O. C=11·73; H=2·45.
$C_8H_{21}N_2I_3S_2Hg$ requires Hg=25·32; I=48·23; C=12·15; H=2·66 per cent.

The compound insoluble in acetone has the formula

$$\begin{array}{c} \text{HgI}\quad\text{Me} \\ \text{NMePh·N:CMe·}\overset{|}{\text{S}}\text{——}\overset{|}{\text{S}}\text{Me} \\ \qquad\qquad\quad\;\; \underset{\text{I}}{|}\quad\;\; \underset{\text{I}}{|} \end{array}.$$

0·1867 gave 0·0449 Hg, 0·1527 AgI, and 0·0870 $BaSO_4$. Hg=25·96; I=48·93; S=6·40.
0·1070 gave 0·0590 CO_2 and 0·0734 H_2O. C=15·06; H=1·39.
0·1227 „ 4·2 c.c. N_2 at 35° and 760 mm. N=3·7.
$C_{11}H_{17}N_2I_3S_2Hg$ requires Hg=24·33; I=46·35; S=7·79; C=16·06; H=2·87; N=3·4 per cent.

Interaction of the above Mercaptide Nitrite and Ethyl Iodide: Formation of the Compound,

$$\begin{array}{c} \text{HgI}\quad\text{Et} \\ \text{NEt}_2\text{·N:CEt·}\overset{|}{\text{S}}\text{——}\overset{|}{\text{S}}\text{Et} \\ \qquad\qquad\quad\;\; \underset{\text{I}}{|}\quad\;\; \underset{\text{I}}{|} \end{array}.$$

(m. p. 73—74°).

0·2316 gave 0·0572 Hg, 0·1960 AgI, and 0·0972 $BaSO_4$. Hg=24·69; I=45·74; S=5·77.*
0·2564 gave 0·0611 Hg. Hg=23·83.
0·1278 „ 0·0703 CO_2 and 0·0296 H_2O. C=15·41; H=2·58.
0·2470 „ 7·8 c.c. N_2 at 31° and 760 mm. N=3·50.
$C_{11}H_{25}N_2I_3S_2Hg$ requires Hg=24·09; I=45·90; S=7·72; C=15·90; H=3·07; N=3·57 per cent.

Phenyl Mercaptide Nitrite and Methyl Iodide: Formation of the Compound, $PhMeS_2,HgI_2,MeI$.

The pure substance was obtained by repeated crystallisation, and was a dull yellow, crystalline powder melting at 90°:

0·4616 gave 0·1252 Hg and 0·4353 AgI. Hg=27·12; I=50·96.
0·1131 „ 0·0551 CO_2. C=13·29.
$C_8H_{11}I_3S_2Hg$ requires Hg=26·6; I=50·66; C=12·77 per cent.

* See footnote, p. 271.

M*

Phenyl Mercaptide Nitrite and Ethyl Iodide: Formation of the Compound, $PhEtS_2,HgI_2,EtI$ (m. p. 59°).

0·2994 gave 0·0774 Hg and 0·2673 AgI. Hg=25·85; I=48·24.
0·1302 „ 0·0740 CO_2 and 0·0282 H_2O. C=15·5; H=1·86.
$C_{10}H_{15}I_3S_2Hg$ requires Hg=25·64; I=48·84; C=15·39; H=1·92 per cent.

Interaction of the Compound, Ph_2S_3Hg, *and Methyl Iodide: Formation of the Compound,*

$$CH_3 \cdot \overset{\displaystyle I}{\underset{\displaystyle HgI}{S}} - \overset{\displaystyle Ph}{\underset{\displaystyle I}{S}} - \overset{\displaystyle Ph}{\underset{\displaystyle I}{S}} \cdot CH_3 .$$

The product was an oil which, on stirring, crystallised. It was washed several times with acetone, when the colour changed to yellowish-white. It was insoluble in acetone, and melted at 111—112°:

0·3150 gave 0·0615 Hg, 0·2915 AgI, and 0·2007 $BaSO_4$. Hg=19·53; I=50·00; S=8·75.
0·1410 gave 0·0902 CO_2 and 0·0390 H_2O. C=17·41; H=3·07.
$C_{14}H_{16}I_4S_3Hg$ requires Hg=20·24; I=51·42; S=9·71; C=17·00; H=1·62 per cent.

It will be noticed that whenever a sulphonium compound contains phenyl groups, it becomes insoluble in acetone.

Mercaptide Nitrite of Thiocarbanilide and Ethyl Iodide: Formation of the Compound, $CEt_2I{\cdot}SEtI{\cdot}HgI$.

In this case, deep purple, needle-shaped crystals were obtained which were soluble in acetone:

0·3083 gave 0·0890 Hg, 0·2920 AgI, and 0·1042 $BaSO_4$. Hg=28·73; I=51·18; S=4·64.
0·1214 gave 0·0552 CO_2 and 0·0232 H_2O. C=12·04; H=2·12.
$C_7H_{15}I_3SHg$ requires Hg=28·09; I=53·51; S=4·49; C=11·80; H=2·11 per cent.

Mercaptide Nitrite of Thiocarbanilide Methyl Ether and Methyl Iodide: Formation of the Compound, Me_2S_2,HgI_2,MeI.

The mercaptide nitrite was heated under reflux with methyl iodide. It was obtained pure by fractional precipitation from a

concentrated solution in acetone by adding ether and repeating the process five or six times, when a fairly good crop was obtained which melted at 160—162°:

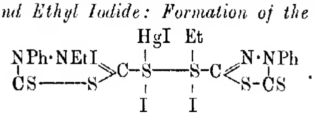
0·3290 gave 0·0791 Hg and 0·3281 AgI. Hg=29·51; I=53·89.
0·1150 „ 0·0221 CO_2 and 0·0218 H_2O. C=5·24; H=2·11.
$C_3H_9I_3S_2Hg$ requires Hg=28·98; I=55·21; C=5·22; H=1·30 per cent.

Mercaptide Nitrite of Thiocarbanilide Ethyl Ether and Ethyl Iodide: Formation of the Compound, Et_2S_2,HgI_2,EtI.

The procedure was almost the same as in the previous instance. On concentrating the acetone solution, a portion crystallised out, which was purified by repeated fractional crystallisation; when pure, it melted sharply at 111°:

0·3127 gave 0·0862 Hg and 0·0978 AgI. Hg=27·57; I=51·46.
0·0861 „ 0·0327 CO_2 and 0·0255 H_2O. C=10·37; H=3·29.
$C_6H_{15}I_3S_2Hg$ requires Hg=27·32; I=52·05; C=10·37; H=3·29 per cent.

2-*Thio*-3-*phenyl*-2:3-*dihydro*-1:3:4-*thiodiazole Disulphide, Mercuric Iodide, and Ethyl Iodide: Formation of the Compound,*



0·3127 gave 0·0512 Hg, 0·2366 AgI, and 0·3026 $BaSO_4$. Hg=16·38; I=40·89; S=13·29.*
0·1574 gave 0·1066 CO_2. C=18·47.
$C_{20}H_{20}N_4I_4S_6Hg$ requires Hg=16·45; I=41·75; S=15·75; C=19·74 per cent.

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* Owing to the tedious process involved in analysis, the values for sulphur and iodine are sometimes too low (compare T., 1916, **109**, 135).

XXVIII.—*The Reaction between Sodium Chloride Solution and Metallic Magnesium.*

By WILLIAM HUGHES.

COLD aqueous solutions of various salts, including sodium chloride, sodium hydrogen carbonate, sodium carbonate, and magnesium sulphate, were found to react with magnesium powder with considerably more speed than one would expect, since cold water acts very slowly on the metal, and solutions of alkali hydroxides not at all.

That the metal slowly dissolves in solutions of its own salts with the formation of hydrogen, the hydroxide, or a basic salt, has been observed by Kippenberger (*Chem. Zeit.*, 1895, **19**, 269), Vitali (*L'Orosi*, 1895, **18**, 289), Lemoine (*Compt. rend.*, 1899, **129**, 291), Bryant (*Chem. News*, 1899, **79**, 75), Kahlenberg (*J. Amer. Chem. Soc.*, 1903, **25**, 380), and Roberts and Brown (*ibid.*, 1903, **25**, 801).

Liberation of the metal together with hydrogen from various salt solutions by magnesium has been described by Commaille (*Compt. rend.*, 1866, **63**, 556), Clowes and Caven (P., 1897, **13**, 221), Divers (P., 1898, **14**, 57), Tommasi (*Bull. Soc. chim.*, 1899, [iii], **21**, 885), and Faktor (*Pharm. Post*, 1905, **38**, 153).

Lohnstein (*Zeitsch. Elektrochem.*, 1907, **13**, 612) found that the action of magnesium on acetic acid was catalysed positively by the addition of some salts and negatively by others.

Knapp (*Chem. News*, 1912, **105**, 253) found that palladium chloride solutions, and Michailenko and Mushinsky (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 181) that the water of crystallisation of certain salts, were acted on by magnesium with the evolution of hydrogen.

EXPERIMENTAL.

In the preliminary experiments, it was found that 0·329 gram of ordinary magnesium powder and 35·3 c.c. of 2*N*-sodium chloride solution gave 291·4 c.c. of a gas at the end of a week. The metal darkened, and a white, gelatinous solid was disseminated throughout the liquid. The greyish-black powder slowly changed to a compact, white solid, but the reaction was not quite complete at the end of seven days. The theoretical yield of hydrogen is 325 c.c. at *N.T.P.*

One c.c. of the original sodium chloride solution and 1 c.c. of the solution which had been acted on by the magnesium gave a

titre of 13·62 c.c. and 13·70 c.c. respectively with silver nitrate. 38·6 C.c. of the gas after absorption for fifteen minutes over freshly prepared alkaline pyrogallol measured 37·5 c.c.

These results were taken to indicate that the gas was hydrogen only, and it was determined to seek a relation, if any, between the rate of evolution of gas and the concentration of the sodium chloride solution.

The method adopted was to add known amounts of magnesium to the different solutions which had been saturated with hydrogen, and to measure the initial velocity of the reaction by reading the volume of hydrogen evolved at 25°, without shaking, at short intervals for a total period of two or three minutes.

Magnesium.—A supply of ordinary magnesium powder, apparently quite bright and free from oxide, was fractionally sifted, and the portion passing through between sieves of 90 and 60 meshes to the inch, respectively, was used. (0·0692 gave 0·3075 $Mg_2P_2O_7$; by Gibbs's method, Mg = 97·03. 0·0258 gave 25·4 c.c. H_2 [dry at 16·5° and 726 mm.] Mg = 96·45 per cent.) Only traces of aluminium and zinc could be detected in the substance. Since the phenomena investigated seemed to depend on the nature of the solutions and not on the small amounts of impurity in the magnesium, it was considered unnecessary to attempt any purification of this reagent.

Sodium Chloride.—Common salt was dissolved in distilled water, filtered, and the solution rendered just alkaline with sodium hydroxide and filtered again. The slightly alkaline solution was evaporated with continual stirring, and the first crop of crystals were well drained and kept over concentrated sulphuric acid.

Water.—Distilled water was redistilled in a glass still which had been previously well steamed out. This water was boiled under diminished pressure previous to being used.

Hydrogen.—This was prepared from zinc and pure sulphuric acid, and purified by passing through lead nitrate solution, silver nitrate solution, a soda-lime tower, and then a set of sodium hydroxide bulbs, and stored over water.

Solutions.—These were made up by weight. The number of molecules of water to each molecule of sodium chloride is represented by c.

Apparatus.—At first the solution—10 cm. deep—was contained in a test-tube, and the hydrogen measured in a nitrometer, the volume being read every fifteen minutes.

The rate was constant in each case for about five hours. The

initial rate was read from the tangent to the curve, and reduced to c.c. at *N.T.P.* per gram of magnesium per hour.

In the second case, a conical flask was chosen as reaction vessel in order to have a smaller hydrostatic pressure on the magnesium. It was fitted with a rubber stopper carrying a delivery tube, *A* (Fig. 1), drawn to a point at the bottom of the flask, for the entry of hydrogen, an exit tube, *B*, which could be closed, and a water manometer, *C*, behind which was fixed a millimetre scale. Selected quill tubing was used in making it, and it was carefully calibrated with distilled water at 25°, and found to be of uniform bore for the part calibrated, namely, the length *DE*. 1 cm. = 0·1880 c.c. at 25°. Twice distilled water saturated with hydrogen was used in the manometer. The weighed magnesium was floated on a capsule on the solution, the volume of which was always 25 c.c., and then the air displaced by, and the solution saturated with, hydrogen through *A* and *B* for not less than ten minutes, all being immersed in the bath. The apparatus was quickly shaken, and simultaneously a stop-watch was started. The volumes of hydrogen read off every half- or quarter-minute were reduced to *N.T.P.*, tabulated (table I), and plotted (Fig. 2, curves 1 and 2). The initial rate was obtained by drawing the tangent as shown. The kind of induction period at the start is much more pronounced with the more concentrated solutions, and is probably due to surface-tension effects, chiefly in the manometer.

FIG. 1.

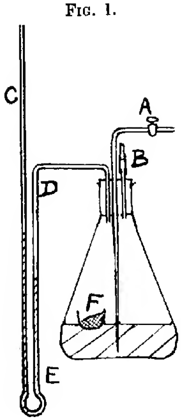


TABLE I.

$c = 30$.

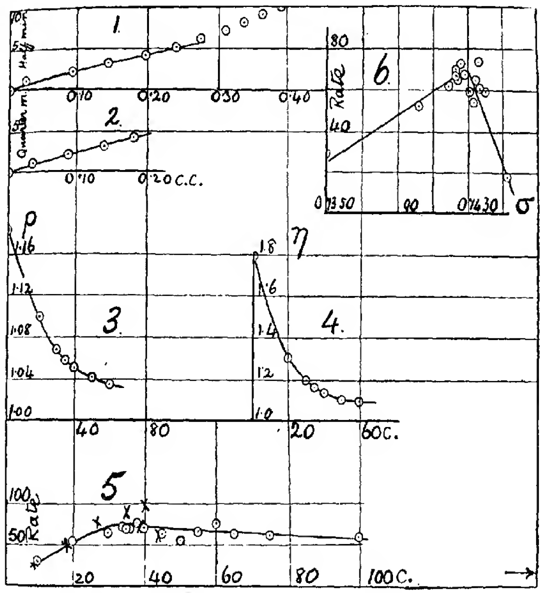
½ minute intervals.	Manometer, Δ (in cm.).	Hydrogen, c.c.	Total pressure (corr.).	Hydrogen, c.c. corrected.
0	0·6	0	—	0
1	0·9	0·15	753·9	0·0256
2	1·7	0·55	754·4	0·0941
3	2·3	0·85	754·9	0·1454
4	2·9	1·15	755·3	0·1969
5	3·4	1·40	755·7	0·2397
6	3·8	1·60	756·0	0·2742
7	4·2	1·80	756·3	0·3086
8	4·5	1·95	756·5	0·3344
9	4·8	2·10	756·7	0·3601
10	5·1	2·25	756·9	0·3860

TABLE I. (*continued*).

$c = 38.$

¼ minute intervals.	Manometer, Δ (in cm.).	Hydrogen, c.c.	Total pressure (corr.).	Hydrogen, c.c. corrected.
0	0·36	0	—	0
1	0·78	0·21	754·0	0·0359
2	1·40	0·52	754·4	0·0889
3	1·98	0·81	754·9	0·1387
4	2·48	1·06	755·2	0·1814

FIG. 2.



The greatest precautions were taken that the solutions of sodium chloride were in each case quite free from acid. Immediately at the end of a determination they reacted alkaline.

The viscosities were determined with an Ostwald viscosimeter, the essential precautions being observed (Applebey, T., 1910, **97**, 2000; from the equation

$$\eta = \eta_{water} \times \frac{\text{density of solution}}{\text{density of water}} \times \frac{\text{time of flow of solution}}{\text{time of flow of water}}.$$

The densities were determined with a pyknometer, the weighings being carried out with a similarly treated counterpoise. These were as shown in table II. The curves are plotted in Fig. 2, 3 and 4.

TABLE II.

Concentration.	$\rho^{25°}_{4°}$.	$\eta_{25°}$.
10	1·184	1·794
20	1·099	1·303
30	1·068	1·198
35	1·058	1·165
40	1·051	1·134
50	1·041	1·101
60	1·034	1·095

In table III are given the initial rates for the different concentrations of sodium chloride solutions.

TABLE III.

Time, hrs.	min.	Temperature.	Pressure, mm. (corr.)	Vol., c.c. (corr.)	c.	Magnesium, Gram.	Rate.	Remarks.
13	30	19°	762·3	31·32	9	0·0984	23·5	First method.
2	20	20	763·9	11·99	18	0·1069	48·1	
	15	22	766·5	1·87	27	0·0995	75·1	
1	20	25	758·7	8·32	45	0·1004	62·2	
	16	24	758·3	2·29	35	0·0985	87·3	
	15	22·5	766·1	2·42	40	0·1004	96·5	
	15	23	767·1	1·58	44	0·1018	62·2	
	16	23	768·3	1·87	39	0·0977	71·6	
	4	25	749·5	0·72	30	0·1165	93·1	Method not accurate enough.
	7	25	749·8	0·18	30	0·0333	46·6	
	3	24·1	749·9	0·45	30	0·1798	50·4	
	2	19·2	749·2	0·51	30	0·1513	100·5	
	1·5	20	749·2	0·37	30	0·1184	124·1	
	0·5	25	749·4	0·0425	30	0·0840	60·7	Second method. Better agreement.
	,,	,,	749·4	0·0710	30	0·1367	64·3	
	,,	,,	750·5	0·0683	30	0·1248	62·3	
	,,	,,	752·8	0·03845	10	0·1590	29·0	
	,,	,,	752·9	0·0664	20	0·1531	52·1	
	,,	,,	753·2	0·0479	30	0·1062	54·2	
	,,	,,	754·8	0·0944	35	0·1702	66·6	
	,,	,,	752·9	0·0684	40	0·1216	67·5	
	0·25	,,	752·3	0·0342	50	0·1507	54·4	Quarter minute intervals.
	,,	,,	757·0	0·0417	60	0·1343	74·6	
	0·5	,,	753·4	0·0135	32	0·0955	17·0	Metal wetted accidentally during bubbling in hydrogen.
	0·25	,,	753·4	0·0513	34	0·1767	69·7	
	,,	,,	753·4	0·0531	36	0·1940	65·7	
	,,	,,	753·4	0·0454	38	0·1478	73·6	
	,,	,,	754·8	0·0343	45	0·1412	59·5	
	,,	,,	754·8	0·0411	55	0·1518	65·0	
	,,	,,	754·8	0·0411	65	0·1581	62·4	
	,,	,,	754·7	0·0386	75	0·1502	61·6	
	,,	,,	755·2	0·0429	100	0·1722	59·7	
	,,	,,	750·6	0·0148	∞	0·1969	18·0	Water only.

These rates are plotted against concentrations in curve 5. The arrow indicates the rate for water ($c=\infty$), and the crosses denote the values obtained with the nitrometer.

Results.

No great accuracy can be claimed for the numerical values, chiefly because the assumption that the total area of equal weights of the sifted magnesium is constant is only approximately true. However, it is evident that curve 5 passes through a maximum at $c=32$; also the surface density of water molecules in contact with magnesium (neglecting surface concentration effects) is given by $\{c\rho/(cM_w+M_s)\}^{\frac{2}{3}}$, where M_w is the molar weight of water, M_s that of sodium chloride, and ρ the density of the solution. Values of this expression ($=\sigma$) have been found for various concentrations and then plotted against the corresponding rates in curve 6. This passes through a maximum for $\sigma=0{\cdot}1426$ about, or $c=37$. One would expect a maximum rate for $c=\infty$ —pure water, since then the magnesium surface would be apparently open to attack by a denser population of water molecules. Again, the values of the viscosity, hydrostatic pressure, and surface tension (Forch, *Ann. Physik*, 1905, [iv], **17**, 744) are each greater for $c=32$ than for weaker solutions, so it seems that the maximum at $c=32$ is not due to any special ease of expulsion of gas through the solution. Further, the specific conductivity of sodium chloride solutions steadily increases to a maximum at the saturation point, so that at $c=32$ the conductivity is not best suited for electrolytic action of impurities in the magnesium to take place.

Conclusions.

(1) Both alkaline and neutral salts positively catalyse the reaction between ordinary magnesium and purified water at the ordinary temperature.

(2) With sodium chloride solutions, the rate of evolution of hydrogen depends on the concentration, the differences being easily detected by the eye. The initial rates for approximately equal areas of magnesium in contact with different concentrations of sodium chloride solutions have been measured, and a maximum has been found for a solution of 32 molecules of water per molecule of sodium chloride.

(3) It is considered that the existence of this maximum points to a specific effect of the dissolved sodium chloride on the water.

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XXIX.—*The Theory of Duplex Affinity.*

By SAMUEL HENRY CLIFFORD BRIGGS.

IN a former paper (T., 1908, **93**, 1564) it was shown how the old conception of duplex affinity can be applied in devising constitutional formulæ for complex inorganic compounds. In a subsequent paper (*ibid.*, 1917, **111**, 253), the theory of duplex affinity was treated from the point of view of the electrical structure of matter. It was assumed that every element is able to exert both positive and negative affinity, positive affinity being a tendency to lose electrons and negative affinity a tendency to attract electrons. A further distinction was made between primary and secondary affinity, the secondary affinity being opposite in sign to the primary affinity, and only coming into action after the primary affinity has been satisfied. By means of these assumptions, it was possible to correlate a number of apparently disconnected phenomena, including the structure and stability of complex compounds, the strength of acids and bases, polymerisation, etc.

The present communication is concerned more particularly with secondary affinity, and some conclusions have been reached which have made it possible to apply the theory of duplex affinity in several new directions.

Secondary Negative Affinity and Secondary Positive Affinity.

As in the previous paper (T., 1917, **111**, 253), Lodge's view (*Nature*, 1904, **70**, 176) that the electrons in an atom are bound to the positive charge, not by a single line of attraction or elastic thread, but by a bundle of a very large number of lines of force, is adopted. For the sake of simplicity, it is supposed that the atoms are spheres, although this is not an essential feature of the general argument. The volumes of the atomic spheres are assumed to be directly proportional to the so-called atomic volumes of the elements.

The term "valency" is used in this paper in a strictly electrochemical sense, in accordance with Sir J. J. Thomson's theory (*Phil. Mag.*, 1914, [vi], **27**, 757).

Consider the case of two univalent atoms A and B, which combine to form a compound AB as the result of the transfer of an electron from A to B, A having positive primary affinity and B having negative primary affinity. Owing to the attraction of B for the electron, a number of lines of force which united the

electron to the positive nucleus of the atom A are broken. Call this number u. Then in the atom B, u lines of force joining electrons in the atom B (previous to its combination with A) to its positive nucleus will be loosened, as a result of the passage of the electron from A to B. Suppose, now, that the compound AB undergoes electrolytic dissociation in solution into the ions $A^{\cdot}$ and B'. The positive nucleus of the cation $A^{\cdot}$ will be able to bind u lines of force from electrons in other atoms, that is to say, the cation $A^{\cdot}$ will have negative affinity, and in this way the secondary negative affinity of the element A arises. The electrons in the anion B', on the other hand, will have u lines of force loosened, and therefore be able to attach themselves to the positive nuclei of other atoms. Consequently, the anion B' has positive affinity, which is the secondary positive affinity of the element B.

Attention must now be directed to a fundamental difference between secondary negative affinity and secondary positive affinity. According to the modern views on the electrical structure of matter, the positive nucleus is situated at the centre of the atom, and its spatial dimensions are extremely minute compared with the volume of the atom as a whole. As we have seen above, however, secondary negative affinity arises from the power of the nucleus to attract lines of force (or electrons). Since the nucleus is at the centre and is so exceedingly small, it follows, so far as the effect on other atoms is concerned, that secondary negative affinity may be regarded as an attractive force distributed equally over the surface of the atomic sphere.

Secondary positive affinity, on the other hand, emanates from the outer electrons (valency electrons or mobile corpuscles) in the atom. The secondary positive affinity cannot therefore be regarded as being equally distributed over the atomic sphere, but must be confined to certain individual electrons or rings of electrons. In other words, secondary negative affinity conforms to Werner's theory of affinity ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., p. 83), whereas secondary positive affinity does not. This difference between secondary negative affinity and secondary positive affinity appears to be of considerable importance in the building up of inorganic compounds, as will be more clearly seen below.

When the ions $A^{\cdot}$ and B' combine to form the molecule AB, some of the loosened lines of force in B will be attached to the positive nucleus of A, as shown by the "ionic formula" $\dashrightarrow A^{\cdot}\leftarrow B'\dashrightarrow$ (T., 1917, **111**, 253). If the number of lines of force thus attached is denoted by v, then in the compound AB the positive nucleus of A is still able to bind u–v lines of force,

whereas the electrons in B have still $u-v$ lines of force loosened and capable of attachment to the nuclei of other atoms. The number $u-v$, therefore, represents the unsaturated secondary negative affinity of A and the unsaturated secondary positive affinity of B, indicated by the dotted arrows in the "atomic formula" $\dashrightarrow A \rightarrow B \dashrightarrow$ and in the "ionic formula" $\dashrightarrow A^{\cdot} \leftarrow B' \dashrightarrow$. (T., 1917, **111**, 253).*

Influence of Atomic Volume.

Since the secondary negative affinity is distributed equally over the surface of the atomic sphere, it follows that when the atomic volume is large, v will be correspondingly small and $u-v$ proportionately large (see p. 286). When the compound AB is dissolved in a dissociating medium, such as water, the molecules of the solvent combine with A and B by means of the unsaturated secondary affinity, thereby bringing about dissociation into the ions $A^{\cdot}$ and B' (compare T., 1908, **93**, 1564). Therefore, if $u-v$ is large, AB will be a strong electrolyte. As shown above, however, $u-v$ is large when the atomic volume of A is large, and this is the reason why the salts of the alkali metals are the strongest electrolytes.

On the other hand, although when the atomic volume of A is large the total unsaturated affinity is correspondingly large, nevertheless the *intensity* of the affinity per unit area of the atomic sphere varies *inversely* as the square of the radius, and is therefore large when the atomic volume of A is small. Consequently, the molecular compounds $(nM \,.\, A)B$, formed by satisfying the free secondary negative affinity of A by the free secondary positive affinity of n molecules of a compound M (such as ammonia or water) (T., 1917, **111**, 253), will be most clearly defined and stable

* Three types of combination are distinguished: (1) Combination due to primary affinity only, as in the formula $\dashrightarrow A \rightarrow B \dashrightarrow$, the passage of the electron from A to B being indicated by the thick arrow pointing from A to B. (2) Combination due to secondary affinity only as seen in molecular compounds, such as $2H_3N \rightarrow CuCl$, the union of the electrons in the nitrogen atom to the positive nucleus of the copper atom being indicated by the thin arrow pointing from nitrogen to copper. (3) Combination due to both primary and secondary affinity as in the non-polar compound $A \rightleftarrows B$.

It should be noted that the formulæ $\dashrightarrow A \rightarrow B \dashrightarrow$ and $A \rightleftarrows B$ represent the limiting cases of the strongest possible electrolyte and the truly non-polar compound respectively. Most compounds will come in between the two formulæ. A compound of intermediate properties might therefore be written $\dashrightarrow A \rightleftarrows B \dashrightarrow$, but it is often convenient to write it as a compound of charged ions rather than of atoms, and in this way the "ionic formula" $\dashrightarrow A^{\cdot} \leftarrow B' \dashrightarrow$ is derived.

when the volume of A is small. As a matter of fact, those elements which form the most stable complex compounds are all found in the depressions of the atomic volume curve (chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, palladium, rhodium, silver, osmium, platinum, iridium, and gold) (see also the work of Ephraim on the effect of the atomic volume of the central atom on the stability of metal–ammonia compounds, *Ber.*, 1912, **45**, 1322).

Conversely, the same reasoning elucidates the somewhat contradictory phenomenon that many of the salts of the alkali metals which are readily soluble in water separate from solution in the anhydrous state. These salts dissolve readily, because of the large value of $u-v$. They do not give stable hydrates, because of the small intensity of the affinity per unit area of the atomic sphere which results from the large atomic volume of the alkali metals.

Non-polar Compounds.

If the two ions $A^{\cdot}$ and B' were to combine in such a way that the secondary affinities completely saturated each other, then the electron would be pulled back into A and the atoms would be held in combination by means of two equal bundles of lines of force, one passing from the nucleus of A to the electrons of B, and the other from the nucleus of B to the electrons in A. That is to say, AB would be a non-polar compound, as shown by the formula $A \rightleftarrows B$.

The conception of secondary negative affinity developed above (p. 279) leads to the following conclusions with regard to the conditions for the formation of non-polar compounds in those cases in which the valency of the element A with primary positive affinity is fully saturated. The conclusions do not, however, apply when A is not exerting its full valency, as the mobile corpuscles still remaining on A introduce complications.

The compounds to be considered, therefore, are those represented by the formula AB_x, in which x varies from 1 to 8 when B is a univalent atom.

When $x=1$, the secondary negative affinity of A is only partly saturated, as already explained (p. 280), because only a part of the spherical surface of A comes under the influence of B. If $x=2$, and A is therefore united to two atoms of B, a larger part of the spherical surface of A is affected, and in general as x increases, more and more of the spherical surface of A is brought under the influence of B. Hence as x increases, the tendency of AB_x to undergo electrolytic dissociation decreases (see p. 280).

The salts of the metals in the earlier groups of the periodic table are therefore the strongest electrolytes, and the electrolytic properties become less marked in the compounds of the metals with higher valency (when they are exerting their full valency).

If, however, AB_x is to be a truly non-polar compound, the secondary negative affinity of A, which is distributed equally over the surface of the atomic sphere, must be completely saturated, and the optimum condition for such complete saturation will be reached when the atoms of B are symmetrically distributed in space around the spherical surface of A.

Since the maximum valency is 8, the number of cases of symmetrical distribution is strictly limited. If B is univalent, x may be 4, 6, or 8, when the atoms of B will be distributed around the spherical surface of A at the corners of a regular tetrahedron, a regular octahedron, and a cube respectively. If B is bivalent, the only possible case is $x=4$, when the B atoms are situated at the corners of a regular tetrahedron. We should therefore expect to find the non-polar properties most strongly marked in compounds having the formulæ AB_4, AB_6, and AB_8 when B is univalent, and AB_4 when B is bivalent.

Since the forces between the molecules of non-polar compounds are small (Thomson, *loc. cit.*, p. 760), such compounds, in addition to their inability to undergo electrolytic dissociation, will also be comparatively volatile and more or less inert. There are several striking instances of compounds with these characteristics in the four classes of substances under discussion.

In the group AB_4 we have the typically non-polar compounds, methane and carbon tetrachloride.

The formula AB_6 is represented by the gaseous sulphur hexafluoride, SF_6, which is almost as inert as nitrogen (Moissan and Lebeau, *Compt. rend.*, 1900, **130**, 865, 984; Berthelot, *Ann. Chim. Phys.*, 1900, [vii], **21**, 205), and by the gaseous tungsten hexafluoride (Ruff and Eisner, *Ber.*, 1905, **38**, 742), WF_6.

Only one compound of the formula AB_8 has hitherto been prepared. This is osmium octafluoride (Ruff and Tschirsch, *Ber.*, 1913, **46**, 929), which boils below 50°, and is a highly stable although reactive substance.

The class AB_4, in which B is bivalent, includes the remarkable tetroxides of ruthenium and osmium, RuO_4 and OsO_4. These compounds both boil at about 100°, and are so completely saturated that they are incapable of combination with alkali hydroxides. Indeed, osmium tetroxide can be distilled off from its solution to which an alkali has been added (compare Ostwald, "The Principles of Inorganic Chemistry," p. 757).

Although symmetry of structure is thus often associated with, and conduces to, non-polarity, it does not follow that all symmetrical compounds will be without polarity, as other factors, such as the relative atomic volumes of A and B, will also exert an influence.

Conversely, when A is *not* exerting its full valency, non-polar combination is possible in substances which are not spatially symmetrical. Thus, according to Thomson (*loc. cit.*), carbon monoxide and nitrous oxide are non-polar compounds.

Other examples given by Thomson bring out the relationship between symmetry and non-polarity in another way. Although both carbon tetrachloride, CCl_4, and methane, CH_4, are truly non-polar, nevertheless chloroform, $CHCl_3$, and methyl chloride, CH_3Cl, are polar compounds.

Werner's Co-ordination Numbers and the Co-ordination Formula.

Suppose the cation $A^{\cdot}$ combines with n molecules of a compound M possessing free secondary positive affinity, such as ammonia or water, to give the complex ion $(nM\,.\,A)^{\cdot}$. Here also the conditions for maximum saturation of the secondary negative affinity of A will involve spatial symmetry in precisely the same way as was seen to apply in the formation of non-polar compounds. The maximum value of n should therefore be either 4, 6, or 8, according to the relative volumes of the atom A and the molecule M; but the maximum value of n is the maximum co-ordination number of the element A, and Werner (*loc. cit.*, p. 52) has shown that this is either 4, 6, or 8. It would appear, also, that the geometrical relationship existing between the volumes of the central atom A and the molecule M is of more importance than the intensity of the affinity in determining the value of the co-ordination number. We find, for example, that barium, with a comparatively large atomic volume, has the maximum co-ordination number 8, as seen in the compound, $(Ba8NH_3)Cl_2$, whereas cobalt, with a much smaller atomic volume, has the maximum co-ordination number 6 in the compound $(Co6NH_3)Cl_3$, in spite of the fact that cobaltic salts have a much greater tendency to combine with ammonia than is shown by barium salts. Similarly, boron, with a very small atomic volume, has the maximum co-ordination number 4 in the compound $(BF_4)H$.

Attention must now be directed to the limiting case in which the secondary negative affinity of A is *completely* saturated by the free positive affinity of M, giving the complex ion $(nM\,.\,A)^{\cdot}$. In what way will the anion B' combine with this complex cation to

give the molecule $(nM.A)B$? In discussing this question, we may suppose that M is a molecule of ammonia. In the former papers (T., 1908, **93**, 1564; 1917, **111**, 253), ammonia was written

$$\begin{array}{l} \rightleftarrows H \\ \leftarrow N \rightleftarrows H\,. \\ \rightleftarrows H \end{array}$$

This formula was derived from the facts (1) that the hydrogen atoms do not undergo electrolytic dissociation in solution in water, and therefore have both primary and secondary affinity saturated, and (2) that the nitrogen atom has free secondary positive affinity, as shown by the ease with which ammonia molecules can combine with the free secondary negative affinity of metals in their salts to give metal-ammonia compounds. From the reasoning developed above, however (p. 280), it is clear that this formula for ammonia, although correct so far as it goes, is not quite complete, because if the nitrogen atom still has $u-v$ lines of force loosened, as expressed by the dotted arrow, then each hydrogen atom must be able to bind $\frac{u-v}{3}$ lines of force to its nucleus. In other words, each hydrogen atom has still a little free secondary negative affinity. Since, however, the free secondary positive affinity in the ammonia molecule is confined to one atom only (the nitrogen atom), it masks the free secondary negative affinity which is distributed over the three hydrogen atoms. In the general case of a compound A_mB_n, in which A and B have free secondary affinity, if m is greater than n the molecule A_mB_n will react as if it had the free secondary affinity of B only. This characteristic will be the more strongly marked the greater the difference between m and n, and it will be all the more intensified the greater the volume of A (the atom with primary positive affinity), and vice versâ. Thus we find that ammonia, water, and potassium chloride react as if they had free secondary positive affinity only in forming complex compounds, whereas cupric chloride, ferric chloride, etc., behave liike substances with free secondary negative affinity.

The complete formula for ammonia should therefore be written

$$\begin{array}{l} \rightleftarrows H \leftarrow \\ \leftarrow N \rightleftarrows H \leftarrow \\ \rightleftarrows H \leftarrow \end{array}$$

in which each hydrogen atom has a little free secondary negative affinity. Returning now to the combination of the complex $(nM.A)^{\cdot}$ with the anion B' to give the salt $(nM.A)B$, we may take the concrete case in which the complex is $(Co6NH_3)^{\cdot\cdot\cdot}$ and the anion is Cl', and assume that the secondary negative affinity of the cobalt atom is *completely* saturated by the free secondary positive affinity of the nitrogen in the six molecules of ammonia.

The only possible way in which the chloride ions can unite with the complex to give the salt $(Co6NH_3)Cl_3$ is by the saturation of the free secondary negative affinity of the eighteen hydrogen atoms by the positive affinity of the chlorine ions. This gives Werner's co-ordination formula $(Co6NH_3)Cl_3$ exactly, in which, according to Werner's phraseology, the chlorine atoms are united to the outer sphere of the complex.

It should be carefully noted, however, that the co-ordination formula only applies to the *limiting* case in which the secondary negative affinity of A is *completely* saturated by nM in the complex $(nM.A)^{\cdot}$. If this saturation is not complete, then the positive nucleus of A will exert an attraction on the electrons in B, as shown by the "ionic formula" $nM \rightarrow A^{\cdot} \leftarrow B' \dashrightarrow$ (T., 1917, **111**, 260). A familiar example is seen in aquopentammine cobaltic chloride, $\left(Co{}^{5NH_3}_{H_2O}\right)Cl_3$, which changes spontaneously into chloropentammine cobaltic chloride, $\left(Co{}^{5NH_3}_{Cl}\right)Cl_2$. Unless the cobalt atom exerts a direct attraction on the chlorine atoms, as shown by the formula ${}^{5NH_3\rightarrow}_{H_2O\rightarrow} Co^{\cdots} \leftarrow Cl_3''' \dashrightarrow$, it is impossible to understand this spontaneous change.

Application of the Theory of Duplex Affinity to Oxygen Compounds.

In the former papers (*loc. cit.*), most of the examples considered were halogen compounds. The development of the theory of secondary negative affinity in the present communication has made it possible to study oxygen compounds from the point of view of duplex affinity in such a way as to bring out some general relationships which are not touched on by other theories of affinity and valency.

Take the case of a metal, M, which forms a series of oxides, MO, MO_2, MO_3, MO_4. In the oxide MO, in which the oxygen atom has received two electrons from the atom M, only part of the atomic sphere of M will come under the influence of the oxygen atom. Hence the secondary affinity of both atoms will be partly unsaturated, and the formula will be

$$\dashrightarrow M \overset{2}{\rightleftharpoons} O \dashrightarrow *.$$

* Instead of denoting the passage of two electrons by two thick arrows $M \rightrightarrows O$, it is more convenient to write one arrow only, with a small figure above to express the number of electrons which it represents, for example, $M \overset{2}{\rightarrow} O$.

When MO is oxidised to give MO_2, a greater part of the spherical surface of M will come under the influence of the oxygen atoms, and the saturation of the secondary affinity will be more complete than in the first oxide, MO. This will apply still more in MO_3, and most of all in MO_4, in which the oxygen atoms are distributed symmetrically in space around M. In MO_4 we therefore have the possibility of complete saturation of the secondary affinity with the production of a non-polar compound. The oxides OsO_4 and RuO_4, referred to above (p. 282), appear to approximate closely to this condition. The four oxides should therefore be written (assuming that MO_4 is non-polar):

$$\dashrightarrow M\overset{2}{\rightleftarrows}O\dashrightarrow \quad \dashrightarrow M\overset{4}{\rightleftarrows}O_2\dashrightarrow \quad \dashrightarrow M\overset{6}{\rightleftarrows}O_3\dashrightarrow \quad M\overset{8}{\rightleftarrows}O_4.$$

It may perhaps be better to write the non-polar oxide $M\leftrightarrows O_4$ rather than $M\overset{8}{\rightleftarrows}O_4$, as the electrons will not have left the M atom in this case.

It should be carefully noted that, since the secondary affinity of M is increased by each addition of an oxygen atom, the saturation of the secondary affinity of the first oxygen atom becomes more complete as oxidation proceeds, because, the secondary affinity of M being distributed equally over the surface of the atomic sphere, the intensity of the affinity present on that part of the spherical surface which comes under the influence of the first oxygen atom will increase with increase in the number of oxygen atoms combined. The *free* secondary affinity of the first oxygen atom will therefore decrease with increasing oxidation of M until in the final, non-polar stage the secondary affinity of the first oxygen atom will be completely saturated. The same reasoning applies, of course, to all the other oxygen atoms as well.

The Hydration of Oxides.—When potassium oxide and water are brought together, there are two ways in which combination may occur. The strongly marked, free secondary positive affinity of the oxygen atom in the potassium oxide may attract the hydrogen atoms of the water, which have slight, unsaturated secondary negative affinity, *or* the unsaturated secondary negative affinity of the potassium may combine with the slight, free secondary positive affinity of the oxygen atom in the water molecule. We may therefore obtain

$$\dashrightarrow K_2O\longrightarrow H_2O\dashrightarrow \quad \text{or} \quad \dashrightarrow H_2O\longrightarrow K_2O\dashrightarrow$$

or perhaps a ring structure $\begin{matrix} O\longrightarrow H_2 \\ K_2\longleftarrow O \end{matrix}$. In potassium, $u-v$ is large, owing to the large atomic volume of potassium (see p. 280), and therefore the unsaturated secondary affinities of the potassium

atoms and the oxygen atoms are large. In water, on the other hand, $u-v$ is small (as seen from the very slight extent to which it is dissociated into hydrogen and hydroxyl ions); hence the unsaturated secondary affinities of the hydrogen atoms and the oxygen atom are small. In each of the three formulæ for K_2O,H_2O, we consequently have the two potassium atoms electrically equal, the two hydrogen atoms electrically equivalent, but the two oxygen atoms very different from each other. The tendency will be for the affinities to be redistributed in such a way as to make the two oxygen atoms also electrically equal, and we therefore have the change $K_2O,H_2O \longrightarrow 2KOH$. Similar considerations will apply to the hydration of other oxides.

Bases and Acids.—When an oxide is hydrated, the product may be either a base or an acid, according to the manner in which it undergoes electrolytic dissociation in solution. If MOH were a base of the strongest possible type, the formula would be written as (I), and if it were the strongest possible type of acid, as (II) (T., 1917, **111**, 253).

$$\dashrightarrow M \rightarrow O \rightleftharpoons H \qquad\qquad M \rightleftharpoons O \leftarrow H \dashleftarrow$$

(I.) (II.)

It has already been shown (p. 286) that increase in the number of oxygen atoms implies a more complete saturation of the secondary affinity of all the oxygen atoms already present in the oxide (anhydrous or hydrated). As the secondary affinity of the oxygen atom of the hydroxyl group becomes more completely saturated by the secondary affinity of M, there is less affinity left to saturate the secondary affinity of the hydrogen of the hydroxyl group, and the free secondary affinity of the hydrogen therefore increases. Consequently, the tendency of the hydrogen atom to be electrolytically dissociated becomes greater, and the structure of the hydroxyl group changes from $\rightarrow O \rightleftharpoons H$ (basic) to $\rightleftharpoons O \leftarrow H \dashleftarrow$ (acidic), with increase in the number of oxygen atoms united to the element M. We therefore have the following general rule:

When a series of oxides of the same element M are hydrated, the hydrate of the highest oxide is the strongest acid (or weakest base). In other words, in a series $M^{OH}_{O_x}$ the greater the value of x the stronger the acidic properties (or the weaker the basic properties).

This rule appears to hold good throughout the periodic table. It is exemplified most clearly in the compounds of the elements in the sixth, seventh, and eighth groups, these being the elements which exhibit the most numerous stages of oxidation. Thus ferrous oxide is basic, ferric oxide less basic (as shown by the greater ease with which ferric salts are hydrolysed), and iron trioxide is acidic. The oxides of chromium form a similar series from the basic chromous and chromic oxides to the acidic chromium trioxide. Manganous oxide is basic, manganic oxide less basic, and manganese dioxide not definitely basic or acidic, whereas manganese trioxide is acidic and dimanganic heptoxide strongly acidic. The oxides of chlorine give rise to a series of acids increasing in strength from the very weak hypochlorous acid, HOCl, to the strong chloric and perchloric acids, $HOClO_2$ and $HOClO_3$. Among nitrogen compounds, hyponitrous acid is very weak, nitrous acid is stronger, and nitric acid is one of the strongest acids known.

The fact that ruthenium and osmium tetroxides are not acidic, although diruthenium heptoxide is strongly acidic, is only an apparent exception to the rule. Owing to their highly saturated character, as has already been shown (p. 282), these compounds are incapable of combination with water, and cannot therefore give rise to hydrated oxides. They therefore do not come within the scope of the rule which applies to hydrated oxides only.

The Hydrogen Ion and the Catalytic Activity of Acids.

From the point of view of the theory of duplex affinity, the hydrogen atom is particularly interesting. According to the views of van den Broek and others (*Ann. Reports*, 1913, **10**, 271), the hydrogen atom is built up of a positive nucleus and one electron (compare Allen, T., 1918, **113**, 390). Consequently, the hydrogen ion $H^{\cdot}$ must consist of a positive nucleus only. The secondary negative affinity of the hydrogen ion must therefore be considered to be concentrated in a "point" of nuclear dimensions rather than distributed over the surface of a (comparatively) very large sphere. The conclusions which have been arrived at in the above discussion from the consideration of the atomic sphere will therefore not necessarily apply to hydrogen. Thus it is not essential for the production of non-polar compounds that the hydrogen atom should be surrounded by negative atoms, as in the cases of sulphur and osmium, for example (see p. 282), methane being a typical non-polar compound.

The identity of the hydrogen ion with the positive nucleus of the hydrogen atom may perhaps ultimately furnish a rational ex-

planation of the catalytic activity of acids, somewhat on the following lines.

Take a molecule $A \rightleftharpoons B$ with a tendency to dissociate according to the equation $AB \rightleftharpoons A + B$. A hydrogen ion (nucleus) if brought into contact with such a molecule will attract to itself some of the lines of force joining the electrons in A to the positive nucleus of B, or the electrons in B to the positive nucleus of A, giving

$$\begin{array}{c} \rightarrow A \rightleftharpoons B \leftarrow \\ \diagdown \; \diagup \\ \mathrm{H} \\ \uparrow \end{array}.$$

The bond uniting A to B will therefore become weaker, and the tendency of AB to dissociate will be increased. It is consequently to be expected that the hydrogen ion will accelerate a chemical change which is already taking place, or even induce a change which would not otherwise occur. Theoretically speaking, other positive ions should act in a similar manner; but since the secondary negative affinity of all other elements is distributed over the surface of a comparatively very large sphere instead of being concentrated in a "point" of nuclear dimension, the catalytic activity of other cations will be exceedingly small compared with that of hydrogen ions.

According to the theory of acids developed in the former paper (T., 1917, **111**, 253), if we neglect unsaturated affinity, the general formula for acids may be written $H \rightleftharpoons X$. If x is the value of the saturated primary affinities and y the value of the saturated secondary affinities in the formula $H \rightleftharpoons X$, y may vary from $y = x$ (the weakest possible acid) to $y = 0$ (the strongest possible acid).

If we now write the formulæ to show the unsaturated affinities, the strongest possible acid has the formula (I) and the weakest possible acid the formula (II).

$$\underset{\text{(I.)}}{\dashrightarrow H \rightarrow X \dashrightarrow} \qquad \underset{\text{(II.)}}{H \rightleftharpoons X}$$

The formula (I) is the case where v (see p. 279) is vanishingly small. Strictly speaking, it is the formula of the dissociated acid ($v = 0$). The unsaturated secondary negative affinity of the hydrogen atom in a molecule of the strongest possible acid (I) is therefore equal to that of the hydrogen ion itself, and as we pass down the series through acids of decreasing strength, the unsaturated secondary negative affinity of the hydrogen atom becomes less until it vanishes, as seen in formula (II). It therefore follows that the undissociated molecule of a very strong acid should also exert catalytic activity, which catalytic activity should decrease

with decreasing strength of the acid, becoming zero in the weakest possible acid (II). It has been shown experimentally that the undissociated molecule of an acid has catalytic activity, the activity diminishing with decreasing strength of the acid (Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 39; Dawson and Powis, T., 1913, **103**, 2135; Dawson and Reiman, *ibid.*, 1915, **107**, 1426; Snethlage, *Zeitsch. physikal. Chem.*, 1913, **85**, 211), but according to Dawson and Powis, the activity of the undissociated acid in some cases is much greater than that of the hydrogen ion. In considering this question, it is necessary to take into account the effect of solvation.

According to the theory of duplex affinity, the chief cause of electrolytic dissociation is the combination of solute and solvent by means of unsaturated secondary affinity (see p. 280). In a solution of an acid we therefore have the following equilibria:

Undissociated molecule + solvent $\rightleftharpoons$ solvated molecule.
Solvated molecule $\rightleftharpoons$ solvated hydrogen ion + solvated anion.
Solvated hydrogen ion $\rightleftharpoons$ solvent + hydrogen ion.
Solvated anion $\rightleftharpoons$ solvent + anion.
Hydrogen ion + anion $\rightleftharpoons$ undissociated molecule of acid.

Take now the extreme case in which the secondary negative affinity of the hydrogen ion is completely saturated by the secondary positive affinity of n molecules of the solvent S (as in a very basic liquid) to give the complex ion $nS.H^{\cdot}$. The positive charge will now be distributed over the comparatively very large outer sphere of the complex (compare p. 284) instead of being concentrated in the nucleus of the hydrogen ion, and the catalytic activity of the complex will therefore be comparatively very small. Solvation will therefore reduce the catalytic activity of both hydrogen ion and undissociated molecule, and the observed catalytic activity of the hydrogen ion and the undissociated molecule in any given experiment will not be proportional to the real catalytic activity of each when unsolvated, but will depend on the degree of solvation of acid and hydrogen ion in accordance with the above-mentioned equilibria. Again, if the solvation is slight, the solvated ion and the solvated molecule may also have appreciable catalytic activity.

These principles are in agreement with the experimental observations on the relative catalytic activities of acids in different media. Water forms complexes much more readily than alcohol; therefore in aqueous solution solvation should be greater than in alcoholic solution, and the catalytic activity of acids should be less in water than in alcohol (compare Kistiakowski, *Zeitsch. physikal. Chem.*,

1898, **27**, 253, and especially Dawson, T., 1911, **99**, 1). Dawson has found that in alcoholic solutions the catalytic activity may be one hundred times as great as in water. Further, the addition of water has been found to decrease the catalytic activity in alcoholic solutions, and this has been shown to be due to combination of the water with the hydrogen ions (Goldschmidt and Udby, *Zeitsch. physikal. Chem.*, 1907, **60**, 728; Lapworth, T., 1915, **107**, 857).

It would be of considerable interest from the point of view of this paper if experiments could be made on the catalytic activity of acids in some truly non-polar medium, such as benzene or carbon tetrachloride. In such a medium, solvation and ionisation would be reduced to a minimum, because non-polar compounds are fully saturated, and therefore unable to combine with the solute. It has been shown, for instance, that benzene at 18° dissolves 2 per cent. of its weight of hydrogen chloride, and that the solution is without electrical conductivity (Falk and Walker, *Amer. Chem. J.*, 1904, **31**, 398). The catalytic activity in a truly non-polar medium would therefore be due to the unsolvated molecule only, and in the case of a very strong acid would probably be very great compared with the activity of the undissociated molecule in aqueous or alcoholic solution.

Conclusion.

For the sake of simplicity, it has been assumed throughout this paper that the atoms are spheres. It must be emphasised, in conclusion, however, that the atomic sphere so often referred to is a purely geometrical conception. We may suppose it to be a sphere described around the atom with the positive nucleus at the centre, and the radius sufficient to include all the constituents of the atom (valency electrons, etc.) within the sphere. The use of this conception is justified by the atomic volume relationships of the elements, and by the fact that the atoms are not capable of interpenetration when endowed with such small amounts of energy as correspond with the motions of thermal agitation of molecules (compare R. A. Millikan, "The Electron," pp. 139, 191).

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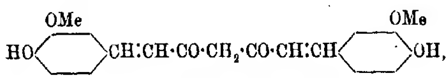
XXX.—*Curcumin*.

By Praphulla Chandra Ghosh.

The work described in this paper was in progress, and in fact completed, before an account of the synthesis of curcumin by Lampe (*Ber.*, 1918, **51**, 1347) appeared.

A portion of the work was devoted to proving the presence of the $\cdot CO\cdot CH_2\cdot CO\cdot$ group, which in any case is now clear from the synthesis, confirming the formula,



previously put forward by Milobendzki, Kostanecki, and Lampe (*Ber.*, 1910, **43**, 2163). The results bearing on this point are therefore given in an exceedingly abbreviated form.

With benzaldehyde, curcumin forms a benzylidene derivative, and it also forms a condensation product with nitrosodimethylaniline.

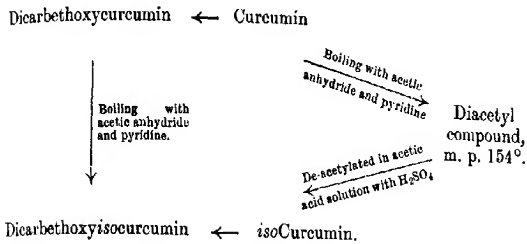
The action of bromine on curcumin and some of its derivatives was also studied with the object of testing the presence of two double bonds.

There were obtained *monobromocurcumin*, $C_{21}H_{19}O_6Br$, *monobromodicarbethoxycurcumin*, $C_{21}H_{17}O_4Br(O\cdot CO_2Et)_2$, *monobromodicarbethoxycurcumin tetrabromide*, $C_{21}H_{17}O_4Br_5(O\cdot CO_2Et)_2$, *dibromodicarbethoxycurcumin tetrabromide*, $C_{21}H_{16}O_4Br_6(O\cdot CO_2Et)_2$, *monobromodiacetylcurcumin*, $C_{21}H_{17}O_4Br(OAc)_2$, *dibromodiacetylcurcumin tetrabromide*, $C_{21}H_{16}O_4Br_6(OAc)_2$, *monobromodimethylcurcumin*, $C_{21}H_{17}O_4Br(OMe)_2$, and *dibromodimethylcurcumin tetrabromide*, $C_{21}H_{16}O_4Br_6(OMe)_2$.

In the course of this investigation, it was discovered that dicarbethoxycurcumin could be converted into dicarbethoxy*iso*curcumin simply by boiling with acetic anhydride and pyridine. This led to the view that one of the two known diacetyl derivatives of curcumin was probably diacetyl*iso*curcumin. Ciamician and Silber described a diacetylcurcumin melting at 169—170°, whilst Jackson prepared an isomeric substance melting at 154° by acetylating curcumin with acetic anhydride and sodium acetate. It was suspected that the latter was probably diacetyl*iso*curcumin, and this suspicion was found to be correct.

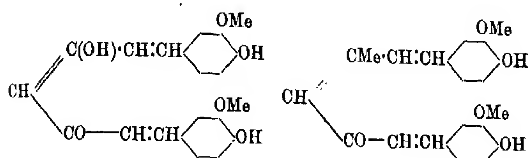
Jackson's compound, which can also be formed by acetylating curcumin with acetic anhydride and pyridine, gives Heller's *iso*curcumin (*Ber.*, 1918, **47**, 887) on hydrolysis. It is therefore quite

easy to convert curcumin into *iso*curcumin. These reactions can be represented graphically, thus:



This simple conversion of curcumin into *iso*curcumin confirms Heller's view that the two substances are geometrical isomerides.

From the ferric chloride reaction, Heller considers that curcumin exists in the enolic form (I), and as there is considerable



(I.) (II.)

resemblance between this formula and that of *divanillylidene-mesityl oxide* (II), the latter has been prepared in the course of this investigation by condensing two molecular proportions of vanillin with one of mesityl oxide by means of hydrochloric acid, and it is intended to compare the absorption spectra of this substance with that of curcumin; similarity of absorption spectra would speak in favour of similarity of molecular configuration.

The condensation of mesityl oxide with some other aromatic aldehydes has been studied, and p-*hydroxybenzylidenemesityl oxide*, o-*hydroxybenzylidenemesityl oxide*, *piperonylidenemesityl oxide*, and *cinnamylidenemesityl oxide* have been isolated.

In connexion with the geometrical isomerism of curcumin and *iso*curcumin, there is some evidence that cinnamylidenemesityl oxide and piperonylidenemesityl oxide exist in two forms.

Most of the compounds examined in the course of this investigation are fluorescent. They are arranged in the following list in the order of their intensity of fluorescence:

Substances arranged in gradually diminishing order of fluorescence.	Solvent in which the greatest intensity is observed.
Curcumin	Chloroform.
Benzylidenecurcumin, $CHPh:C(CO{\cdot}CH:CH{\cdot}C_6H_3[OMe]{\cdot}OH)_2$	Acetone.
p-Hydroxybenzylidenemesityl oxide, $OH{\cdot}C_6H_4{\cdot}CH:CH{\cdot}CO{\cdot}CH:CMe_2$	Toluene
o-Hydroxybenzylidenemesityl oxide	Toluene.
Dicarbethoxycurcumin, $CH_2(CO{\cdot}CH:CH{\cdot}C_6H_3[OMe]{\cdot}O{\cdot}CO_2Et)_2$	Acetone.
Diacetylcurcumin, $CH_2(CO{\cdot}CH:CH{\cdot}C_6H_3[OMe]{\cdot}OAc)_2$	Acetone.
Divanillylidenemesityl oxide	Acetone.
Monobromocurcumin, $CHBr(CO{\cdot}CH:CH{\cdot}C_6H_3[OMe]{\cdot}OH)_2$	Acetone.
Monobromodicarbethoxycurcumin tetrabromide, $CHBr(CO{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_3[OMe]{\cdot}O{\cdot}CO_2Et)_2$	Chloroform.
Dibromodicarbethoxycurcumin tetrabromide, $CBr_2(CO{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_3[OMe]{\cdot}O{\cdot}CO_2Et)_2$	Chloroform.

From these observations, it may be inferred that (1) auxochromic groups, (2) the labile hydrogen atoms, (3) the double bonds, and (4) the symmetry of the molecule increase fluorescence, but are not the invariable factors of fluorescence.

EXPERIMENTAL.

Benzylidenecurcumin, $C_6H_5{\cdot}CH:C_{21}H_{18}O_6$.—A current of dry hydrogen chloride was passed through a mixture of benzaldehyde (0·5 gram), curcumin (1·8 gram), and alcohol (40 c.c.) cooled with ice. The colour became dark violet, probably owing to the formation of curcumin hydrochloride, and in about a day the whole of the curcumin dissolved and the colour changed to orange-red. After forty-eight hours, the mixture was poured into ice-cold water, when a greenish-yellow precipitate was obtained which could not be crystallised. It was purified by solution in acetic acid and fractional precipitation by sodium acetate (sample I), and subsequently in the same way by precipitation from an alcoholic solution by water (sample II). It is soluble in alcohol, acetic acid, acetone, or chloroform, shrinks slightly at 170°, and melts at 200°:

I. 0·1000 gave 0·2695 CO_2 and 0·0486 H_2O. C=73·5; H=5·4.
II. 0·1104 ,, 0·2965 CO_2 ,, 0·0527 H_2O. C=73·25; H=5·3.
$C_{28}H_{24}O_6$ requires C=73·68; H=5·26 per cent.

Condensation Product of Curcumin and Nitrosodimethylaniline, $N(CH_3)_2{\cdot}C_6H_4{\cdot}N:C_{21}H_{18}O_6$.—One part of curcumin and one part of nitrosodimethylaniline were dissolved in alcohol, two parts of zinc

chloride were added, and the mixture was warmed for a few minutes on the water-bath. When the colour became brown, the product was precipitated by water. A good deal of tarry matter was dissolved by treatment with 30 per cent. acetic acid. The residue could not be crystallised, but was purified by fractional precipitation from acetic acid solution by water. The substance obtained in this way is fairly readily soluble in alcohol, acetic acid, or acetone, shrinks at 98°, and melts and decomposes at 144—145°. Two fractions obtained by precipitation with water from acetic acid solution had the same melting point, and gave the following results on analysis:

I. 0·1502 gave 7·6 c.c. N_2 at 30° and 760 mm. N=5·7.
II. 0·1430 „ 7·1 c.c. N_2 „ 29° „ 758 mm. N=5·61.
$C_{29}H_{28}O_6N_2$ requires N=5·8 per cent.

Monobromocurcumin, $C_{21}H_{19}O_6Br$.—Half a gram of curcumin was dissolved in 35 c.c. of warm chloroform, the solution cooled until curcumin began to separate, and 4·5 c.c. of a 5 per cent. solution of bromine in chloroform were then gradually added, avoiding rise of temperature. The solution became quite clear on the first addition of the bromine solution (1 c.c.), and hydrogen bromide was evolved. After ten minutes, air was blown through the mixture to drive off the chloroform, and the residual emulsion was rubbed with a little alcohol. Needle-shaped crystals of monobromocurcumin separated, which were soluble in alcohol, chloroform, acetic acid, acetone, or toluene, shrank at 131°, and melted at 136°:

0·1187 gave 0·0510 AgBr. Br=18·2.
$C_{21}H_{19}O_6Br$ requires Br=17·9 per cent.

Monobromodicarbethoxycurcumin, $C_{21}H_{17}O_4Br(O{\cdot}CO_2Et)_2$, prepared in a similar way from dicarbethoxycurcumin, crystallises from much alcohol in needles melting at 165—170°:

0·1172 gave 0·0382 AgBr. Br=13·87.
$C_{27}H_{27}O_{10}Br$ requires Br=13·47 per cent.

Monobromodicarbethoxycurcumin tetrabromide,
$C_{21}H_{17}O_4Br_5(O{\cdot}CO_2Et)_2$.
—Dicarbethoxycurcumin (1 gram) was dissolved in the minimum quantity of cold chloroform and treated with 40 c.c. of a 2·5 per cent. solution of bromine in the same solvent. After remaining at the ordinary temperature for one and a-half hours, the chloroform was driven off by a current of air. The product was extracted successively with boiling ethyl and methyl alcohols, leaving a residue which could not be crystallised, but was purified by dissolving in chloroform and fractionally precipitating with alcohol. It is

sparingly soluble in alcohol or light petroleum, and melts and decomposes at 209—210°. Different fractions gave the same analytical results:

0·1397 gave 0·1438 AgBr. Br=43·8.

$C_{27}H_{27}O_{10}Br_5$ requires Br=43·9 per cent.

Dibromodicarbethoxycurcumin tetrabromide,

$C_{21}H_{16}O_4Br_6(O\cdot CO_2Et)_2$,

was obtained by brominating dicarbethoxycurcumin in cold chloroform solution with excess of bromine. It separated from alcohol in colourless crystals, softening at 148° and melting at 152°. It remains unchanged on boiling with water:

0·1278 gave 0·1460 AgBr. Br=48·61.

$C_{27}H_{26}O_{10}Br_6$ requires Br=48·48 per cent.

Monobromodiacetylcurcumin, $C_{21}H_{17}O_4Br(OAc)_2$.—Ciamician and Silber's diacetylcurcumin was brominated in cold chloroform solution with a little more than the theoretical quantity of a chloroform solution of bromine (as in the preparation of monobromodicarbethoxycurcumin). It crystallises from alcohol in needles melting at 173—174°, and is brighter in colour than diacetylcurcumin itself:

0·1162 gave 0·042 AgBr. Br=15·38.

$C_{25}H_{23}O_8Br$ requires Br=15·03 per cent.

Dibromodiacetylcurcumin tetrabromide, $C_{21}H_{16}O_4Br_6(OAc)_2$, was obtained by brominating diacetylcurcumin in cold chloroform solution with excess of bromine, and was crystallised from alcohol. It melts and decomposes at 80—83°:

0·1477 gave 0·1785 AgBr. Br=51·43.

$C_{25}H_{22}O_8Br_6$ requires Br=51·45 per cent.

Monobromodimethylcurcumin, $C_{21}H_{17}O_4Br(OMe)_2$, was obtained by treating dimethylcurcumin in cold chloroform solution with a little more than the theoretical quantity of bromine. It crystallises from alcohol in needles melting at 140—141°:

0·1200 gave 0·0468 AgBr. Br=16·6.

$C_{23}H_{23}O_6Br$ requires Br=16·49 per cent.

Dibromodimethylcurcumin tetrabromide, $C_{21}H_{16}O_4Br_6(OMe)_2$.—Dimethylcurcumin dissolved in chloroform was treated with excess of bromine, when hydrogen bromide was evolved, and, after half an hour, the chloroform was evaporated. This substance could not be crystallised, but was purified by precipitation from its hot alcoholic solution with water. Distinct fractions possessed the same melting point (softens at 96°, melts at 102—104°) and gave

identical analytical results. It is soluble in chloroform or acetic acid:

0·1120 gave 0·1437 AgBr. Br = 54·6.

$C_{23}H_{22}O_6Br_6$ requires Br = 54·87 per cent.

*Conversion of Dicarbethoxycurcumin into Heller's Dicarbethoxy-*iso*curcumin.*

A mixture of 1 gram of dicarbethoxycurcumin, 10 c.c. of acetic anhydride, and 1 c.c. of pyridine was digested at the boiling point for forty-five minutes. Alcohol (6 c.c.) and a little water were added to the cooled mixture, and the supernatant liquid was decanted from the viscous mass which thus separated. From the latter, by stirring with 2 c.c. of glacial acetic acid, a solid product was obtained, and this when crystallised from alcohol melted at 142°, which is identical with the melting point given by Heller for dicarbethoxy*iso*curcumin.

Found: C = 63·0; H = 5·5

$C_{27}H_{28}O_{10}$ requires C = 63·28; H = 5·46 per cent.

Acetylation of Curcumin with Acetic Anhydride and Pyridine.

Curcumin was digested with acetic anhydride and pyridine under the same conditions as described in the last paragraph, and a solid product isolated. The yellow solid obtained in this way was fractionally crystallised from acetic acid. The first fraction (which was only a minor portion) melted at 169—170°, and was found to be identical with Ciamician and Silber's diacetylcurcumin (mixed melting point). The second fraction (major portion) melted at 154°, and this, it is interesting to note, is identical with that given by Jackson for his diacetyl compound obtained by means of acetic anhydride and sodium acetate.

Found: C = 66·4; H = 5·23.

$C_{25}H_{24}O_8$ requires C = 66·37; H = 5·3 per cent.

Deacetylation of Diacetylcurcumin (m. p. 154°) *and Isolation of Heller's* iso*Curcumin.*

One gram of this diacetyl compound was dissolved in 15 c.c. of acetic acid, 1 c.c. of sulphuric acid (D 1·84) added, the mixture warmed for a minute, cooled, and poured into water. The yellow precipitate was dried on porous porcelain and extracted with hot benzene. The benzene solution, on cooling, deposited the substance as a yellow, amorphous powder, soluble in cold alcohol, acetic acid, acetone, ethyl acetate, or chloroform, sintering at 140° and melting

about 280°. There could be little doubt that this compound was identical with Heller's *iso*curcumin:

0·1130 gave 0·2822 CO_2 and 0·0571 H_2O. C=68·1; H=5·6.

$C_{21}H_{20}O_6$ requires C=68·4; H=5·43 per cent.

p-*Hydroxybenzylidenemesityl oxide*,

$OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:C(CH_3)_2$.

—To an alcoholic solution of 2·4 grams of *p*-hydroxybenzaldehyde and 1 gram of mesityl oxide, 1·5 grams of zinc chloride were added, and the liquid was boiled for two hours. The solution, after concentration, was poured into water, causing the deposition of oily drops, which became crystalline on agitation. On recrystallisation from alcohol, yellow crystals were obtained, which melted at 120° and dyed yellow shades on chrome-mordanted wool:

0·1210 gave 0·3590 CO_2 and 0·0784 H_2O. C=80·91; H=7·2.

$C_{13}H_{14}O_2$ requires C=81·25; H=7·36 per cent.

o-*Hydroxybenzylidenemesityl oxide* was prepared in a similar way to the corresponding *p*-hydroxy-compound. The crude product separated as an oil, which was obtained crystalline by dissolving in aqueous potassium hydroxide, allowing to remain for a few days, and precipitating with hydrochloric acid. The substance dissolves with a very beautiful orange-red colour in potassium hydroxide solution:

0·1000 gave 0·2970 CO_2 and 0·0667 H_2O. C=81·0; H=7·42.

$C_{13}H_{14}O_2$ requires C=81·25; H=7·36 per cent.

Piperonylidenemesityl oxide,

$CH_2:O_2:C_6H_3\cdot CH:CH\cdot CO\cdot CH:C(CH_3)_2$.

—Piperonal (2·6 grams) and mesityl oxide (2 grams) were dissolved in alcohol, and alcoholic potassium hydroxide was added to render the solution fairly alkaline. The mixture was boiled for a few minutes, when an orange-coloured substance began to separate. On cooling, this solid was collected, dissolved in acetic acid, and reprecipitated with water, when it melted at 130—135° (*A*). This proved to be a mixture of two substances melting at 148—153° and 175—178° respectively, which can be separated either by fractional precipitation by alcohol from acetic acid or by extraction with alcohol, in which the substance of higher melting point is scarcely soluble. The hot alcoholic extract, on cooling, deposits the substance, which melts at 148—153° (*B*). The insoluble residue, dissolved in chloroform and fractionally precipitated by alcohol (the first fraction being rejected), melted at 175—178° (*C*):

(*A*) 0·1000 gave 0·2662 CO_2 and 0·0558 H_2O. C=72·6; H=6·2.
(*B*) 0·1150 „ 0·3040 CO_2 „ 0·0580 H_2O. C=72·1; H=5·6.
(*C*) 0·1021 „ 0·2710 CO_2 „ 0·0533 H_2O. C=72·4; H=5·8.

$C_{14}H_{14}O_3$ requires C=73·0; H=6·08 per cent.

Cinnamylidenemesityl oxide,

$$C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}C(CH_3)_2,$$

was prepared in the same way as the above piperonylidene compound. On cooling the reaction mixture, some viscous substance was deposited, from which the supernatant liquid was decanted and poured into water. The semi-solid mass was dissolved in acetic acid and precipitated with alcohol. It melts and decomposes at 180—182° (α). Addition of water to the filtrate caused the separation of a second substance, which melted and decomposed at 88° (β). Both the α- and β-compounds were soluble in alcohol, chloroform, acetone, or toluene, but could not be crystallised from any of these solvents. Experiment showed that these compounds were interconvertible; the former (α) on boiling with acetic acid for two to three minutes and adding water to the solution gave the β-compound melting at 88°, whereas the latter on boiling with alcohol for about five minutes gave, on cooling the solution thus obtained, a deposit of the α-compound melting at 180—182°.

The α-compound is less readily soluble in alcohol than the β:

(α) 0·1082 gave 0·3365 CO_2 and 0·0670 H_2O. C=84·4; H=6·8.
(β) 0·1494 ,, 0·4610 CO_2 ,, 0·0808 H_2O. C=84·1; H=6·0.
$C_{14}H_{15}O$ requires C=84·4; H=6·4 per cent.

Divanillylidenemesityl oxide (II, p. 293).—A current of dry hydrogen chloride was passed into an ice-cooled alcoholic solution of 2·6 grams of vanillin and 1 gram of mesityl oxide, when the liquid became deep blue. After two days, the solution was poured into cold water, the precipitate collected and triturated with sodium acetate solution. The brown, amorphous powder obtained in this way could not be crystallised, and was purified by fractional precipitation from acetic acid with water solution. It is soluble in alcohol, chloroform, or acetone, softens at 165°, and melts at 178°. Distinct fractions obtained by the above described method gave identical analytical results:

I. 0·1200 gave 0·316 CO_2 and 0·067 H_2O. C=71·8; H=6·2.
II. 0·1065 ,, 0·282 CO_2 ,, 0·059 H_2O. C=72·21; H=6·1.
$C_{22}H_{22}O_5$ requires C=72·1; H=6 per cent.

I take this opportunity of thanking Prof. B. N. Das for his kind help and encouragement during the progress of the work.

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XXXI.—*The Rotatory Dispersive Power of Organic Compounds. Part IX. Simple Rotatory Dispersion in the Terpene Series.*

By Thomas Martin Lowry and Harold Helling Abram.

In a paper on "The Form of the Rotatory Dispersion Curves," published in 1913 (T., **103**, 1067), it was shown:

(*a*) That the rotatory dispersion in a large number of simple organic compounds may be expressed by the formula

$$\alpha = k/(\lambda^2 - \lambda_0^2),$$

where k is the "rotation constant" and λ_0^2 is the "dispersion constant" of the substance.

(*b*) That this formula can be applied both to magnetic and to natural rotatory powers.

(*c*) That a very simple method of testing the form of the dispersion curves is to plot the reciprocals of the rotatory powers against the squares of the wave-lengths. When the simple dispersion formula is valid, the observations will plot out to a straight line.

The validity of this simple dispersion formula was established in several ways. Thus:

(1) Twenty-five hydrocarbons, alcohols, and acids for which the ratio $\alpha_{4358}/\alpha_{5461} = 1{\cdot}636$ were grouped together, and their *magnetic* dispersion ratios were averaged for six different wave-lengths; these averages showed a remarkable agreement with the ratios calculated by means of the simple dispersion formula.

(2) In the same way the *optical* dispersion ratios of eight secondary alcohols, for which $\alpha_{4358}/\alpha_{5461} = 1{\cdot}651$, were found to agree closely with ratios calculated by the simple formula.

(3) A few optical and magnetic rotations of larger magnitude showed a similar close agreement in individual cases, without the necessity for averaging which arises when the readings are small.

(4) In the case of α- and β-methyl glucosides, very concordant results were obtained when the two constants of the simple equation were calculated (*a*) from the mercury readings α_{4358} and α_{5461}, (*b*) from the cadmium readings α_{5086} and α_{6438} (Lowry and Abram, *Trans. Faraday Soc.*, 1914, **10**, 108).

These earlier observations showed that the simple dispersion formula can be applied very generally to compounds of simple structure, such as the optically active secondary alcohols, which contain only a single asymmetric carbon atom and also to com-

pounds such as the glucosides which contain several asymmetric carbon atoms associated with the simplest possible radicles, for example, hydrogen, hydroxyl, and the like. An opportunity has, however, occurred recently of testing the validity of this same simple formula in the case of a large number of optically active compounds in which these elements of simplicity in the molecular structure are conspicuously absent. The striking results of this further test form the subject of the present communication.

The new data now under consideration were provided by the observations of Prof. Rupe, who in continuation of earlier experiments on the "Influence of Constitution on the Rotatory Power of Optically Active Substances" (*Annalen*, 1903, **327**, 157; 1909, **369**, 311; 1910, **373**, 121; 1913, **395**, 87, 136; 1913, **398**, 372; 1914, **402**, 149) has published a series of measurements of the optical rotatory power of (1) twelve derivatives of methylenecamphor, (2) menthol and eleven of its esters, (3) myrtenol and eleven of its esters, (4) three hydrocarbons derived from citronellaldehyde, (5) camphor, pulegone, and carvone (*Annalen*, 1915, **409**, 327). Unlike the previous series of measurements, which were confined to observations with sodium light, the last series included, in the case of almost every compound, readings for four different wave-lengths in the visible region of the spectrum. It was therefore possible to study, not only the optical rotatory power of the various compounds, but also the character of their rotatory dispersion.

The four wave-lengths, selected from a continuous spectrum, were $\lambda=6563$, 5898, 5463, and 4861, corresponding closely with the Fraunhofer lines: $C=6563$, $D=5893$, $F=4861$, and the green mercury line Hg 5461. In order to preserve a convenient sequence of lettering, these four wave-lengths were described as C, D, E, and F; but, as the symbol E has long been applied to the Fraunhofer line of wave-length 5270, the symbol Q is used below for the green (quicksilver) line in the series, which thus becomes C, D, Q, F.

The various substances were examined either in the pure state as liquids at 20° or dissolved in benzene at 20°, since this solvent was found to have no very great influence on the rotatory powers; several substances were examined both in the pure state and in solution.

When the experimental work was approaching completion, the data were handed over for detailed analysis to Dr. A. Hagenbach, Professor of Physics in the University of Basle. The important deductions which he was able to make are set out in a paper on "Rotatory Dispersion in Homologous Series" (*Zeitsch. physikal.*

Chem., 1915, **89**, 570). The chief points of this paper are as follows:

(1) The dispersion ratio α_F/α_C is practically constant in each series of closely-related compounds. Compounds which differ in any marked degree from the average are regarded as "relatively anomalous."

(2) A similar statement may be made in reference to all the six ratios α_F/α_C, α_F/α_D, α_F/α_Q, α_Q/α_C, α_Q/α_D, α_D/α_C, as was shown by tabulating these ratios for (i) eight derivatives of methylene-camphor, (ii) menthol and seven of its esters, (iii) three hydro-carbons from citronellaldehyde.

(3) It follows, therefore, that if the dispersion law for one member of the series be given by the equation $\alpha=\phi(\lambda)$, the rotatory dispersion in every compound may be expressed by equations, such as:

$$[\alpha_1]=C_1\phi(\lambda).$$
$$[\alpha_2]=C_2\phi(\lambda).$$
$$[\alpha_3]=C_3\phi(\lambda).$$

This proportionality of rotatory powers was demonstrated by tabulating the ratios α_2/α_1, α_3/α_1, α_4/α_1, etc., in each of the three series of compounds.

Attempts were made to determine, mainly by graphical methods, the nature of the unknown function $\phi(\lambda)$. Thus, the equations of Biot,

$$\alpha=B/\lambda^2,$$

and of Stefan,

$$\alpha=A+B/\lambda^2,$$

were tested by plotting α against $1/\lambda^2$. Boltzmann's equation:

$$\alpha=A/\lambda^2+B/\lambda^4 \quad \text{or} \quad \alpha\lambda^2=A+B/\lambda^2,$$

was tested by plotting $\alpha\lambda^2$ against $1/\lambda^2$. In neither case was an exact linear law disclosed. The equations of Lommel, and the two-term equation which Drude used to express the rotatory power of quartz, could not be tested in this way; but the empirical equations:

$$\alpha=A+B/\lambda^n \quad \text{and} \quad \log\alpha=A+B/\lambda$$

were tested by plotting $\log\alpha$ against $\log 1/\lambda$ and against $1/\lambda$; subsequently, $\log\alpha$ was also plotted against λ, and α against $1/\lambda$ (*Annalen*, 1915, **409**, 349, 351), but again without disclosing any simple linear relation between these quantities. The nature of the function in the equation $\alpha=\phi(\lambda)$ thus remained still undiscovered. The present paper serves to supply this deficiency by showing that in almost every case the new dispersion data can be

expressed by a simple equation of the type first put forward by Drude.

The fact that Drude's equation was not used by Hagenbach, and in general failed during many years to secure the practical recognition which it deserves, may be accounted for in two ways. In the first place the equation was put forward, as an approximation only, in a very general form:

$$\alpha = \Sigma \frac{k_n}{\lambda^2 - \lambda_n^2},$$

containing an indefinite number of arbitrary constants. The arbitrary constants, λ_1^2, λ_2^2, λ_3^2, . . ., in the denominator were deduced from measurements of refractive dispersion, and it was not even suggested that they could be derived (in a still more satisfactory way and often with much greater exactness) from the rotations themselves. In the second place, Drude demonstrated the validity of his equation only in one single case, namely, that of quartz, the equation for which took the form

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k}{\lambda^2}.$$

No data whatever were given for optically active liquids, and the magnetic rotatory dispersion in carbon disulphide and in creosote (!) was expressed by a different formula, also depending on measurements of refractive dispersion. The first extensive practical application of Drude's formula was therefore made less than six years ago in the second paper of the present series.

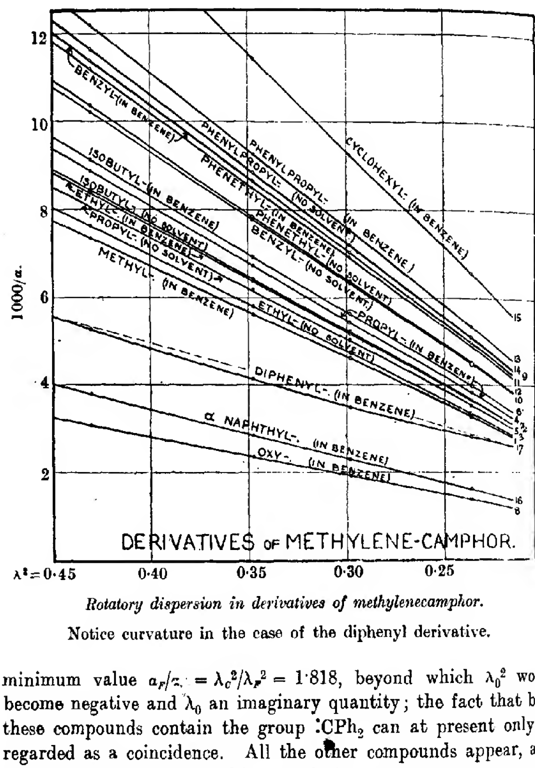
The easiest (although perhaps the least exact) method of testing the simple dispersion law, $\alpha = k/(\lambda^2 - \lambda_0^2)$, is to plot the reciprocals of the rotations against the squares of the wave-lengths. The dramatic effects which are produced by plotting $1/\alpha$ against λ^2 are shown by comparing the straight lines of Figs. 1 to 4 with the broken lines* or curves which were given by all other methods of plotting. It is specially remarkable that plotting α against $1/\lambda^2$ (Stefan's formula) should give curves, where plotting $1/\alpha$ against λ^2 (Drude's formula) gives very exact straight lines. These lines indicate clearly that, where half a dozen other relationships have failed, the simple Drude formula gives at once a satisfactory expression of the experimental data.†

* Hagenbach appears to have plotted his curves on the assumption that the "E" line used by Rupe was the Fraunhofer line α_{5270}, and not the mercury line α_{5461}.

† More exact data may perhaps compel the use of additional terms, as in the case of quartz, which requires one, two, or three terms, according to the range and accuracy of the data employed, but there are no indications of this in the data examined hitherto.

A marked exception occurs in the case of pulegone, which gives a smooth, full curve, and evidently shows "complex" rotatory dispersion. Diphenylmethylenecamphor, $C_{10}H_{14}O{:}CPh_2$, the dispersion ratios of which are much lower than those of all the related compounds, gives a curve; so also does menthyl β-phenylcinnamate, $C_{10}H_{19}O{\cdot}CO{\cdot}CH{:}CPh_2$, the rotatory dispersion of which must be complex, since the dispersion ratio, $\alpha_F/\alpha_C = 1{\cdot}72$, falls below the

FIG. 1.



Rotatory dispersion in derivatives of methylenecamphor.

Notice curvature in the case of the diphenyl derivative.

minimum value $\alpha_F/\alpha_C = \lambda_C^2/\lambda_F^2 = 1{\cdot}818$, beyond which λ_0^2 would become negative and λ_0 an imaginary quantity; the fact that both these compounds contain the group $:CPh_2$ can at present only be regarded as a coincidence. All the other compounds appear, as a result of this rough graphical analysis over a narrow range of wave-lengths, to give simple rotatory dispersion.

A more exact test of the dispersion formula is given by numerical calculation. The following table shows that the specific rotations,

observed and calculated, of a series of typical compounds lie well within the range of possible experimental errors.

TABLE I.

Specific Rotations, Observed and Calculated.

Ethylidenecamphor,* $[\alpha]=47{\cdot}322/(\lambda^2-0{\cdot}0829)$.

Obs.	136·37°	178·58°	219·31°	308·49°
Calc.	136·05	178·58	219·55	308·49
O−C	+0·32	±	−0·24	±

Hydroxymethylenecamphor,* $[\alpha]=22{\cdot}843/(\lambda^2-0{\cdot}0874)$.

Obs.	66·53	87·66	108·57	153·41
Calc.	66·53	87·70	108·26	153·41
O−C	±	−0·06	+0·33	±

Benzylmethylenecamphor, $[\alpha]=33{\cdot}431/(\lambda^2-0{\cdot}0887)$.

Obs.	97·87	129·00	156·26	226·50
Calc.	97·75	129·00	156·39	226·50
O−C	+0·12	±	−0·13	±

Menthol,* $[\alpha]=15{\cdot}068/(\lambda^2-0{\cdot}0236)$.

Obs.	37·01	46·58	54·78	70·84
Calc.	37·01	46·47	54·82	70·84
O−C	±	+0·11	−0·04	±

Menthyl benzoate,* $[\alpha]=29{\cdot}364/(\lambda^2-0{\cdot}0255)$.

Obs.	72·41	91·10	107·76	139·30
Calc.	72·46	91·10	107·59	139·30
O−C	−0·05	±	+0·17	±

Myrtenol, $[\alpha]=14{\cdot}700/(\lambda^2-0{\cdot}0316)$.

Obs.	36·83	46·49	55·04	71·81
Calc.	36·83	46·48	55·09	71·81
O−C	±	+0·01	−0·05	±

Myrtenyl benzoate, $\alpha=11{\cdot}505/(\lambda^2-0{\cdot}0341)$.

Obs.	29·01	36·67	43·51	56·90
Calc.	29·01	36·67	43·52	56·90
O−C	±	±	−0·01	±

* Dissolved in benzene.

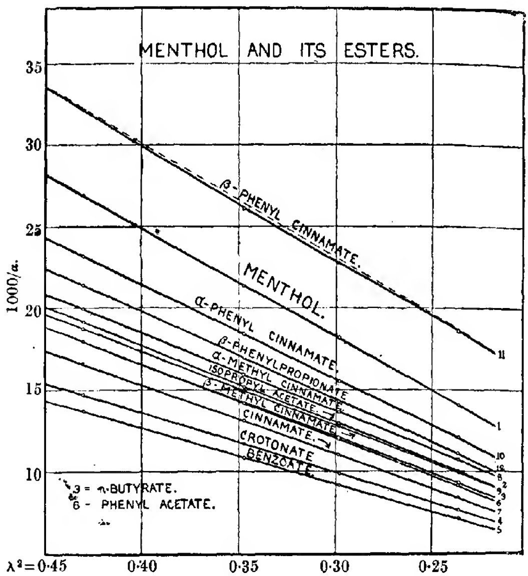
In view of the fact that the readings for solutions in benzene were multiplied by ten to convert them into specific rotations, whilst the others were approximately doubled, the agreement shown above is practically perfect.

Even clearer evidence of the validity of the simple dispersion formula is afforded by a study of the average dispersion ratios observed and calculated for groups of related compounds. Three such groups were averaged by Hagenbach, namely:

(*a*) Eight derivatives of methylenecamphor (dissolved in benzene), $\alpha_F/\alpha_C = 2{\cdot}310$.

(*b*) Seven esters of menthol (pure or in benzene), $\alpha_F/\alpha_C = 1{\cdot}920$.

FIG. 2.



Rotatory dispersion in menthol and its esters.

Notice curvature in the case of β-phenylcinnamate.

(*c*) Three derivatives of citronellaldehyde (in the pure state), $\alpha_F/\alpha_C = 1{\cdot}991$.

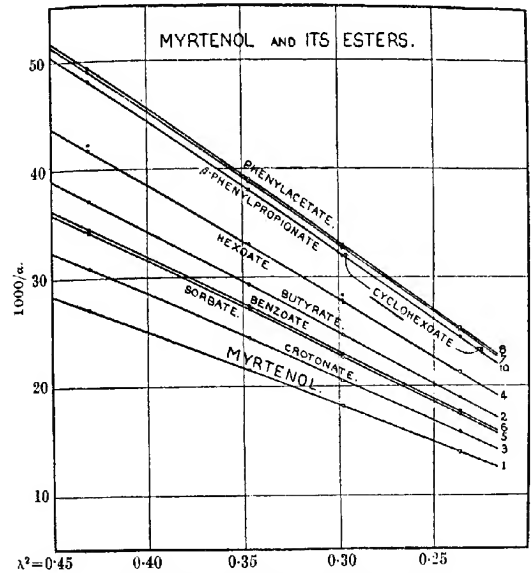
To these there are now added average ratios for:

(*d*) Six derivatives of methylenecamphor (in the pure state), $\alpha_F/\alpha_C = 2{\cdot}303$.

(*e*) Menthol and seven esters (dissolved in benzene), $\alpha_F/\alpha_C = 1{\cdot}911$.

(*f*) Myrtenol and eight esters (in the pure state), $\alpha_F/\alpha_C = 1{\cdot}958$. The close agreement between the observed and calculated values of these ratios is shown in table II.

Fig. 3.



Rotatory dispersion in myrtenol and its esters.

Table II.

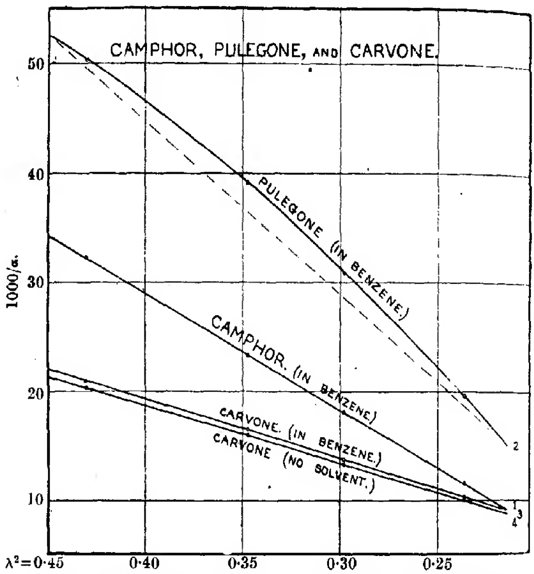
Dispersion Ratios, Observed and Calculated.

		α_F/α_C.	α_F/α_D.	α_F/α_Q.	α_Q/α_C.	α_Q/α_D.	α_D/α_C.	
(*a*)	Obs.	2·310	1·751	1·415	1·633	1·237	1·319	$\lambda_0^2 =$
	Calc. ...	2·310	1·752	1·418	1·629	1·236	1·318	0·0879
(*b*)	Obs.	1·920	1·529	1·294	1·488	1·181	1·259	$\lambda_0^2 =$
	Calc. ...	1·921	1·529	1·294	1·484	1·181	1·257	0·0250
(*c*)	Obs.	1·991	1·561	1·313	1·515	1·188	1·274	$\lambda_0^2 =$
	Calc. ...	1·992	1·569	1·316	1·513	1·191	1·269	0·0401
(*d*)	Obs.	2·303	1·756	1·423	1·619	1·234	1·312	$\lambda_0^2 =$
	Calc. ...	2·303	1·748	1·417	1·626	1·234	1·318	0·0871
(*e*)	Obs.	1·911	1·521	1·289	1·482	1·180	1·256	$\lambda_0^2 =$
	Calc. ...	1·911	1·522	1·292	1·479	1·179	1·255	0·0227
(*f*)	Obs.	1·958	1·550	1·306	1·499	1·186	1·264	$\lambda_0^2 =$
	Calc. ...	1·958	1·550	1·306	1·499	1·186	1·264	0·0334

This agreement is nearly as close as in the case of the data by which the validity of the simple Drude formula was first established, and even the largest differences are usually less than the average errors of the individual ratios. The "simple" character of the rotatory dispersion could therefore only be called in question if data were available of greater exactness or over a wider region of the spectrum.

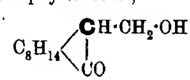
A further opportunity of testing the validity of the simple dis-

FIG. 4.



Rotatory dispersion in derivatives of camphor pulegone and carvone.
Notice curvature in the case of pulegone.

persion law is provided by the inclusion in a more recent paper by Prof. Rupe (*Helv. Chim. Acta,* 1918, **1**, 452) of dispersion data for four samples of camphylcarbinol,



a compound containing three asymmetric carbon atoms as com-

ponents of a complex ring system. The agreement between the observed and calculated rotations is shown in table III.

TABLE III.

Rotatory Dispersion in Camphylcarbinol.

First sample, $[\alpha]=15{\cdot}980/(\lambda^2-0{\cdot}10220)$.

	$\lambda=6563$	5898	5463	4861
Obs.	48·64°	65·24°	81·57°	119·17°
Calc.	48·64	65·05	81·43	119·17
O−C	±	+0·19	+0·14	±

Second sample, $[\alpha]=15{\cdot}213/(\lambda^2-0{\cdot}10223)$.

Obs.	46·31	62·11	77·67	113·48
Calc.	46·31	61·93	77·53	113·48
O−C	±	+0·18	+0·14	±

Third sample, $[\alpha]=15{\cdot}252/(\lambda^2-0{\cdot}10239)$.

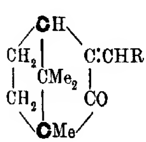
Obs.	46·45	62·22	77·74	113·90
Calc.	46·45	62·13	77·79	113·90
O−C	±	+0·09	−0·05	±

Fourth sample, $[\alpha]=16{\cdot}10/(\lambda^2-0{\cdot}10304)$.

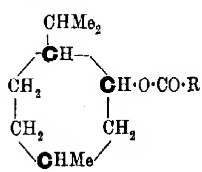
Obs.	49·13	65·73	82·44	120·82
Calc.	49·13	65·76	82·39	120·82
O−C	±	−0·03	+0·05	±

It will be observed that the sample having the highest rotatory power, which was also probably the purest, gives a remarkably close agreement, the differences being in opposite directions and amounting only to a few hundredths of a degree, or about 1 part in 2000. This exact agreement suggests that the simple dispersion law may be of value as a test of purity, and that deviations from it may in some cases justify a further examination of the chemical composition of the material used for the measurements.

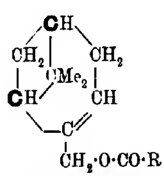
It is of interest to notice the chemical character of the compounds to which the "simple" dispersion formula has now been applied. They are as follows:



1. Methylene camphors.



2. Menthol esters.



3. Myrtenol esters.

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}\mathbf{C}HMe{\cdot}CH{:}CHR$.

4. Hydrocarbons from citronellaldehyde.

Nearly all are complex ring compounds or loaded with double bonds. The fact that the simple formula applies to compounds of such complex structure is remarkable evidence of the broad and sound basis on which the formula rests.

Characteristic Wave-lengths.—In Drude's simple equation, the rotatory dispersion is defined completely by the "dispersion constant" λ_0^2; this is the square of a wave-length, which is that of a hypothetical absorption band, usually in the ultra-violet region of the spectrum. This wave-length defines the whole course of the dispersion curve, and is independent of the particular wave-lengths used to determine it; thus the value of λ_0^2 may be deduced equally well from the mercury ratio $\alpha_{4358}/\alpha_{5461}$, from the cadmium ratio $\alpha_{5086}/\alpha_{6438}$, or from the ratio α_F/α_C derived from the data now under discussion. A preliminary study of these data by Prof. Rupe had, however, disclosed the fact that, in the case of the methylene-camphors, $\alpha_F/\alpha_C = \alpha_D$, whilst in the case of the citronellaldehyde hydrocarbons, $\alpha_F - \alpha_C = \alpha_C$, that is, for each series there is a "characteristic wave-length," λ_a (*Zeitsch. physikal. Chem.*, 1915, **89**, 581), for which the rotation is equal to the difference between the rotations for the F and C lines. This wave-length is not a fundamental constant of the dispersion curve like the λ_0^2 of Drude's equation, since it depends on the two standard wave-lengths, for example, F and C, which are selected as determining the difference; but it usually lies within the limits of the visible spectrum and affords a picturesque method of setting out the essential features of the dispersion curve. By assuming the validity of Stefan's formula, Hagenbach showed that this wave-length can be deduced from the expression

$$\frac{1}{\lambda_a^2} = \frac{\alpha_C}{\alpha_F - \alpha_C}\left\{\frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2}\right\} - \frac{1}{\lambda_C^2},$$

or, taking in all the four rotatory powers,

$$\frac{1}{\lambda_a^2} = \frac{\alpha_F - \alpha_C - \alpha_E}{\alpha_C - \alpha_D}\left\{\frac{1}{\lambda_C^2} - \frac{1}{\lambda_D^2}\right\} - \frac{1}{\lambda_E^2}.$$

Drude's equation, on the other hand, which is the one that actually fits the curves, gives for the "characteristic wave-length" the expression

$$\lambda_a^2 = \frac{\lambda_C^2 - (n-2)\lambda_F^2}{(n-1)^2} = \frac{0{\cdot}4307 - 0{\cdot}2363(n-2)}{(n-1)^2},$$

where n is the dispersion ratio α_F/α_C. Thus, for the citronell-aldehyde hydrocarbons, for which $n = 2{\cdot}00$, this equation gives $\lambda_a^2 = \lambda_C^2$, as was observed experimentally when it was found that $\alpha_F - \alpha_C = \alpha_C$.

Constant Rotatory Dispersion in Homologous Series.—In the compounds now under consideration, new radicles are introduced into the molecule at points which are separated from the asymmetric carbon atoms by a considerable chain, including in every case either an oxygen atom or a double bond. A constant dispersion ratio is therefore observed from the beginning, and any substance of which the rotatory dispersion differs largely from the average of the series is noteworthy and exceptional. The only conspicuous exceptions amongst some thirty-six compounds under consideration in the present research were found in two substances containing the group $\vdots CPh_2$. These have now been shown to differ from the others also in giving complex instead of simple dispersion curves, so that the rule appears to apply without exception to all compounds showing simple rotatory dispersion.

A different state of affairs prevails, however, in the secondary alcohols of Pickard and Kenyon, which have a "growing chain" attached directly to the asymmetric carbon atom. The dispersion is here always simple, but the dispersion constant varies in the different series, and only assumes a steady value in each series when the "growing chain" of carbon atoms has definitely established itself as the heaviest radicle attached to the asymmetric carbon atom (Lowry, Pickard, and Kenyon, T., 1914, **105**, 101). The lowest homologues usually show an exceptionally high rotatory dispersion, but this is not accompanied by any change in the type of the dispersion curve, and is therefore entirely distinct from the "anomalous rotatory dispersion," of which an exact definition was given in a former paper of the present series (T., 1915, **107**, 1195). It would be a real misfortune if substances which are perfectly normal in their rotatory dispersion were to be regarded even as "relatively anomalous" whenever they happen to differ slightly from their homologues, and it is hoped that this unnecessary and misleading description will be abandoned.

Summary.

It is shown that the simple dispersion formula

$$\alpha = k/(\lambda^2 - \lambda_0^2)$$

can be applied to express the rotations produced by a large number of compounds of the terpene series, including (*a*) derivatives of methylenecamphor, including camphylcarbinol, (*b*) menthol and its esters, (*c*) myrtenol and its esters, and (*d*) hydrocarbons derived from citronellaldehyde. Pulegone, and two compounds containing the group $\vdots CPh_2$, show complex rotatory dispersion.

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[*Received, March 20th*, 1919.]

XXXII.—*A New Sector Spectrophotometer.*

By SAMUEL JUDD LEWIS.

IN a paper by the author on "The ultra-violet absorption spectra of blood sera" (*Proc. Roy. Soc.*, 1917, [*B*], **89**, 327), it was stated that the work described had been done with two sector spectrophotometers, that these were not adequate to the exacting nature of the investigation, although they were the best and most modern instruments available, and that a new photometer to the author's design was under construction. That apparatus has now been in use for several months, and the purpose of this paper is to describe it. A short account of the method of using such instruments is given in the reference mentioned above.

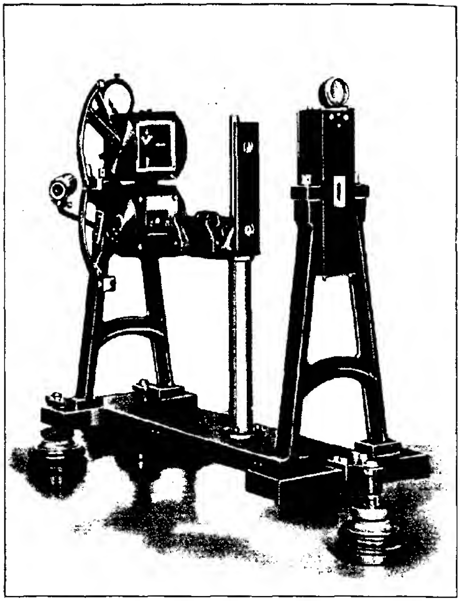
As was the case with the work detailed in the paper cited, the present development of the sector spectrophotometer has been generously supported by the Beit Research Fund Committee, the trustees of a fund which has been placed at the disposal of the British Homeopathic Association by Mr. Otto Beit for purposes of scientific research.

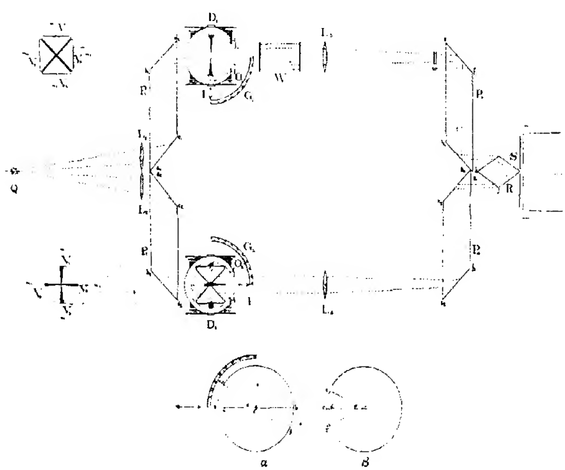
The new instrument was designed by the author in 1915 with a view to meeting the requirements of the work on blood serum. No instrument can be unnecessarily refined for this, and should it be desired to employ the method of ultra-violet absorption spectrography for clinical purposes, whether for blood serum or for any other substances, an instrument which is at once trustworthy and easy to manipulate is essential. Incidentally, an instrument which fulfils these conditions should satisfy most of the demands of scientific research and bring the practice of ultra-violet absorption spectroscopy within the range of applied chemistry. Unless or until the ideals set out are attained, absorption spectroscopy can have little more than academic significance; but perfect, easily adjustable spectrophotometers may be expected in course of time to occupy a place in the general laboratory not less important than that filled by the polarimeter or the refractometer.

Among the objects aimed at in the new design were the following:

(*a*) The utmost accuracy and refinement in the resulting spectra, because for the serum work it is required to discover with certainty very small differences of detail in the absorption curve, as explained in the paper cited.

(*b*) To work quickly as well as accurately, since it is necessary to undertake the examination of a serum at very short notice, and there is no reasonable opportunity of revising the observation, as




D₁
W
P₁
Q
S
R
P₂
G₂
D₂
a
β

[To face page [illegible]

the serum will usually have changed in character by the time the absorption curve is drawn; this presumes quick and perfect adjustment of the instruments.

(*c*) To maintain this excellent adjustment throughout an experiment, or to restore it from time to time during the progress of an observation, without the necessity of other disturbances.

(*d*) Precise quantitative values for the extinction coefficients, since the amplitude of the curve has important significance.

(*e*) To attain this high standard, and yet to be able to use the one spectrograph alternately with the photometer and for other purposes as circumstances may require.

The photograph exhibits the general appearance of the new photometer; it exposes the vanes in the upper sector, the front of the sector box having been removed; also only one platform bearing a tube carrier is shown. The arrangement of parts is displayed in the diagram.

Q represents a suitable lamp, light from which falls on the two lenses L_1, L_2, which render the light parallel. These pencils of light pass through the face a_1b_1 in the reflecting prism P_1 and through the face a_2b_2 in the reflecting prism P_2 in the manner shown, and are reflected approximately at right angles by the inclined faces a_1c_1 in prism P_1 and a_2c_2 in the prism P_2, so that in each case the light follows a course parallel to the main axis of the prism to a second inclined face b_1d_1 in prism P_1 and b_2d_2 in prism P_2, where it is reflected again at right angles.

The parallel beam reflected from b_1d_1 passes through the sector D_1, the diaphragm O_1, and the lens L_3 to the inclined face e_1f_1 in reflecting prism P_3, where it is reflected at right angles along the main axis of the prism on to the inclined face g_1h_1, where it is again reflected at right angles and passes out of the prism on to the face ki of the rhomb R placed in front of the slit S of the spectrograph, or, in the absence of the rhomb, directly on to the slit.

The pencil from b_2d_2 undergoes similar treatment, and eventually passes out of the photometer on to the face kj of the rhomb.

The rhomb may be dispensed with if the pencils of light are directed so as to fill the angles of the prisms at g_1 and g_2, provided that one prism slightly overlaps the other, as shown in the figure, so that the prominent edge may define the line of juxtaposition. It will be seen that any stray parts of the pencils of light would be reflected or escape out of the field.

The essential part between the two prisms in either path is the sector D_1, D_2, capable of cutting off any desired portion of the light passing along that path.

It should be observed that the prisms and sectors are enclosed in dust-proof metal boxes provided with quartz windows.

The sector system is placed in a part of the path where the light is parallel. It consists of four vanes, V_1, V_2, V_3, V_4, as shown in the side elevations in the figure. Each vane has two edges at right angles, and when the four vanes are disposed to one another in one plane, so that the four angles meet at a point, the system is closed and no light can pass. This arrangement is represented in the upper path in the figure. The common point of the four angles is on the optic axis, to which the plane is at right angles. Each vane can be turned by means of suitable mechanism about its bisectors, m_1, m_2, m_3, m_4. When all the vanes are turned simultaneously through an angle of 90° about their respective bisectors, light can pass in the direction of the optic axis without any interruption except that caused by the slight obstruction due to the thickness of the material of the vanes, as shown in the figure for the lower path. By turning the vanes through any other given angle about their bisectors, a known proportion of the light may be allowed to pass. Each of the four vanes is carried on a wheel, by means of a spindle which coincides with the bisector of the vane and also forms the axle of the wheel. These wheels are mounted on the outside of the walls of the box enclosing the sector at right angles to one another, and fit into one another by bevelled cogs. They move simultaneously, and the fitting is so close that back-lash is reduced to an insignificant minimum. The amount of rotation of the vanes is measured by a pointer, I, mounted on the front wheel and moved against an arc graduated in half degrees from 0 to 90.

A diaphragm or stop, O_1, O_2, is placed in front of each sector to reduce the section of the beam of light to suitable dimensions, say 9 mm. in diameter when the observation tubes or cells have a lumen of 12 mm.

In order to correct the error caused by the obstruction due to the thickness of the material of the vanes, their edges are reduced to knife edges, and the thickness along the bisector is graduated from the minimum at its extremity at the optic axis to what is necessary, say 1 mm., at a distance of 10 mm. The two sides of each vane are equally made, and each of the four surfaces is plane or concave. Hence a section through a vane at right angles to its bisector has the form of a rhombus having two very obtuse and two very acute angles; also a section which includes the bisector has the form of an isosceles triangle.

It follows that when the sector system is open, as shown in the lower path in the figure, the obstruction or shadow produced by

each vane has the form of a geometrical sector of known dimensions, and therefore the sectional area of the pencil of light passing through the sector system is reduced by four times the area of one small sector shadow; also, each of the four apertures has the form of a geometrical sector.

Compensation for this reduction in area is made by employing for the path in which the light is to be of whole, or 100 per cent. intensity, that is, for the path in which the substance under observation is placed, a diaphragm the aperture of which is appropriately larger than that of the diaphragm in the other path. In the author's instrument, the diameter of the larger aperture is 9·3 mm. and that of the smaller 9·0 mm. These diaphragms are loose and may be used with either sector, according to whether it is desired to use the upper or lower sector.

The only limitation to this arrangement is that the sectors do not operate for those angles which are included by the small angle covered by the thickness of the vanes. In the author's instrument this is 2·6°, so that the range of operation is from 2·6° to 90°.

The lenses L_3, L_4, placed between the sectors and the second set of prisms, focus the light on the slit, the focus being that for light of a wave-length of about 3000.

The edge of the rhomb is placed close to the slit, so that the two pencils of light when they emerge from either side of it into the slit may be at the focus of the collimating lens; the line of juxtaposition between the two spectra is thus very clearly defined without the least overlapping or intervening space, with the result that the lines in the two spectra, whether visual or photographic, can be compared for their relative intensities at the best advantage.

The cell containing the substance under observation is placed in the parallel beam of light between the sector and the central lens; room is provided for tubes up to 100 mm. in length, and tubes of this length were used successfully in an investigation relating to Lambert's law. As the pencil of light is 9·3 mm. in diameter, it is desirable for long tubes that the lumen of the tube should be at least 12 mm. in diameter, so as to avoid serious reflection from the inner walls of the tube. When the lumen is small and the layer of substance thin, it may be placed in the convergent beam immediately in front of the prism P_3, as shown at *w*, and a still smaller cell might be interposed between the prism P_3 and the face *ki* of the rhomb, but only with due regard to existing conditions. Inasmuch as the system in the lower path of light is identical with that in the upper, the cell may be placed in the lower with equal advantage, or, as explained later, cells may be placed in both beams simultaneously.

The new instrument is characterised chiefly by its sectors; these are distinguished both in their construction and in the principles upon which they operate. In comparison and contrast with other sectors, they accommodate the whole beam of light, and not merely half, as is the case with some others; this enables exposures to be reduced to one-half in order to produce a photograph of the same intensity; the exposures being continuous, calibration of the photographic plate is avoided; the direct function of the new sectors is to cut down the intensity of the light, and not to do so indirectly by altering the exposure, as is the case with the Hilger instrument; the sector is still, which is a great convenience. The whole aperture of the sector system is made up of four sector-shaped apertures arranged diagonally about the optic axis, that is, they are disposed at an angle of 45° to the vertical. This has the advantage of utilising all parts of the circular beam of light in proper proportion, whatever the magnitude of the effective aperture at the moment. In this it differs from the iris and other forms of stop or sector, which reduce the intensity of the light by cutting down the light from the periphery of the beam inwards, or by cutting it down in some other way which assumes that every part of the field is equally illuminated. Under the conditions of ordinary practice, this assumption lacks sufficient justification where precise photometry is required.

The size of the sector aperture is measured in terms of the angle which it forms at the optic axis. The angle 45° represents an aperture of 100 per cent., and the angle formed at the optic axis by the shadow cast by one half of a vane in any given position is ϕ. Hence the sector aperture is proportional to $45° - \phi$. This method of measuring the size of the aperture is exceedingly convenient both for simplicity of calculation from the angle θ, which is read on the graduated arc, and for the fact that apertures of any odd value may be produced at will. This will become evident from the following explanation of the manner of calculation.

When the vane *acb* in the figure (α) (front elevation) is turned through an angle θ, as measured by the graduated arc, so as to take up the position *ecf*, each half of the vane *ec* or *cf* creates a sector-shaped shadow to a beam of light in the direction of the arrow; $e'd'$ is a projection of *ed*. It is shown again in the figure (β) in side elevation, where $e'd'$ is the projection of *ed*. If the beam of light were rectangular in section, the shadow would be triangular in shape ($e'd'o$) and proportional in area to $\sin\theta$, since *ed*, which subtends the angle θ, is equal to e_1d_1, which subtends the angle ϕ at the optic axis, O, for ed' and $d'o$ are equal, since they form the right angle in the isosceles triangle $ed'o$; therefore $ed/ed' =$

$e'd'/d'o$, that is, $\sin\theta = \tan\phi$, whence θ being known, ϕ may be found directly from the tables.

The beam of light, however, is circular in section; hence the area of any sector in the circle is proportional to the angle which it contains, that is, to ϕ for the shadow and $45° - \phi$ for the sector aperture.

Only one-eighth of the whole circular aperture has been considered, but it will be seen on cancelling common factors that the whole aperture at any moment is measured by $45° - \phi$, where $45°$ is taken to represent the fully open sector. It is convenient to express the apertures as percentages of the whole aperture, that is, as $\frac{(45-\phi)100}{45}$. The percentage apertures and values for $\log I/I'$ corresponding with each half-degree on the graduated arc have been calculated by Miss Gartha Thompson, to whom the author is indebted for valuable assistance throughout the inquiry. Examples are given in the following table:

θ.	Sin θ or tan ϕ.	ϕ.	$45-\phi$.	Sector aperture, per cent. $\frac{(45-\phi)100}{45}$	Log I/I', $\log\frac{45}{45-\phi}$.
10	0·1736482	9·85108	35·14892	78·11	0·1073
25	0·4226183	22·90981	22·09019	49·08	0·3091
40	0·6427876	32·73241	12·26759	27·27	0·5644
40·5	0·6494480	33·00163	11·99837	26·67	0·5740
41	0·6560590	33·27239	11·72760	26·07	0·5839
55	0·8191520	39·32269	5·67731	12·62	0·8991
70	0·9396926	43·21918	1·78082	3·958	1·4026
80	0·9848078	44·56143	0·43857	0·975	2·0111
80·5	0·9862856	44·60441	0·39559	0·870	2·0559
81	0·9876883	44·64512	0·35488	0·789	2·1031
85	0·9961947	44·89078	0·10922	0·243	2·6150
85·5	0·9969173	44·91155	0·08845	0·197	2·7065
88	0·9993908	44·98255	0·01745	0·0388	3·4114

It is evident that the values in the table can be applied to graduating the arc on the instrument so that it may read directly in terms of $\log I/I'$, as has been done with other instruments. This is convenient where it is intended to use the instrument for routine work only, but for versatile research, and especially where it is desired occasionally to elaborate a particular part of an absorption curve, the freedom conferred by the ordinary scale and tables will be appreciated. There is, however, no difficulty in providing both scales on the same arc.

The effect produced by the size of the shadow cast by the vane being a function of the sine of the angle through which the vane has been turned is significant. From the above figures, it will be

seen that the difference in the sector aperture produced by a constant difference of 15° in θ decreases continuously, thus:

		Per cent.
Between 10° and 25° the aperture decreases by	(78·11—49·08)	29·03
„ 25° „ 40° „ „ „ „	(49·08—27·27)	21·81
„ 55° „ 70° „ „ „ „	(12·62— 3·96)	8·66
„ 70° „ 85° „ „ „ „	(3·96— 0·24)	3·72

Again, for half-degree intervals in θ:

Between 20° and 20·5° the aperture decreases by	(58·03—57·09)	0·94
„ 40° „ 40·5° „ „ „ „	(27·27—26·67)	0·60
„ 80° „ 80·5° „ „ „ „	(0·975—0·879)	0·096
„ 85° „ 85·5° „ „ „ „	(0·243—0·197)	0·047

For any of the apertures of small size, it is evident, therefore, that a movement of the pointer on the arc over one or more divisions alters the size of the aperture by only a small fraction, so that any probable error in construction or manipulation can have no detectable effect on the measurement of the size of the aperture.

The possibility of regulating the size of the small apertures with such precision is a valuable advantage, since it is with these that much of the more important and delicate work is done.

In an investigation of uric acid, undertaken to see if it obeyed Lambert's law, it was proved that the results for all the small apertures down to 0·29 per cent. (reading 84·5° on the graduated arc and giving the value 2·53 for $\log I/I'$) harmonised perfectly with those found for the larger apertures. The still smaller ones were not quite so true, owing to a slight imperfection in the setting of the vanes, but this can be avoided in reproducing the instrument.

The instrument is absolute in all its measurements. That it is not only so, but that it is also precise, follows from the examination of a standard piece of glass which was supplied by Messrs. Adam Hilger with their photometer for calibration purposes. The figures obtained are tabulated below. The two sets of values for $\log I/I'$ are as follows: (*a*) those obtained by the new photometer; (*b*) the figures given by Hilger:

Wave-length.	(*a*).	(*b*).
2751	0·281	0·278
2636	0·665	0·610
2564	0·919	0·888
2478	1·318	1·330
2435	1·605	1·608
2389	1·970	1·940

Of the two methods, the one with the new photometer has the advantage of being direct and of not depending on the assumption

that photometry in the ultra-violet is uniform with that in the visible region and on the use of accessory apparatus, as in the method published by Hilger. In any case, the two series of results are sufficiently similar to one another to call for a discussion as to which is the more accurate expression of the phenomena.

Considerable advantage is gained by having two sectors which are equal in all respects, as in the new photometer. As already stated, the substance can be placed in the first and second paths alternately, so that any slight imperfections in the sectors or in any part of the optical train will express themselves in opposite senses in the two series of spectra; also the work will be confirmed and experimental error corrected at the same time. The mean of the two closely concordant results must be a very near approximation to the truth.

Further, opportunity is provided for eliminating the effect of the solvent directly. Most of the solvents, alcohol, for example, give feeble absorption spectra which spoil the accuracy of the extinction coefficients of the dissolved substance under investigation. It is not altogether satisfactory to correct the absorption constants of the solution by subtracting those due to the solvent, which have been ascertained separately, and in any case it is laborious to do so; for example, it is not safe to assume that a standard curve for absolutely pure alcohol applies to commercially pure spirit. Indeed, some of the impurities commonly occurring in rectified spirit are strongly absorbent of ultra-violet light. It is better to place in the one path a tube of the solution, and in front of the constant sector a similar tube filled with the same solvent as that used in making the solution. It is a good plan to have a tube of the given solvent in each of the two paths when adjusting the instrument, and then to replace the solvent in one of them by the solution in question. It is perhaps unnecessary to do so, but it lends a sense of satisfaction, while it adds little or nothing to the experimental work. It is certain that the differences then observed in the two spectra are due entirely to the substance in the dissolved state, and hence its absorption curve can be derived directly. There is, however, the possibility of the absorption spectrum being modified by the association of the solute with the solvent, but that is a matter for other inquiry in each particular case and does not affect either the general truth of the proposition or the operation of the instrument.

STAPLE INN BUILDINGS,
HIGH HOLBORN, W.C. 1. [*Received, March 3rd, 1919.*]

XXXIII.—*The Formation and Stability of* spiro-*Compounds. Part II. Bridged* spiro-*compounds Derived from* cyclo*Hexane.*

By Christopher Kelk Ingold and Jocelyn Field Thorpe.

Introduction.

(A) *General.*

In Part I. of this series (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080) a comparison was drawn between the conditions of formation and the stability of the bromo-esters of $\beta\beta$-dimethylglutaric acid and *cyclo*hexane-1 : 1-diacetic acid. These two acids contain respectively the structures I and II, and the object with which

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}C\\C\end{matrix} \qquad\qquad CH_2<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}C\\C\end{matrix}$$

(I.) (II.)

these comparisons were made may be indicated by reference to Figs. (i) and (ii), which are drawn to correspond with structures I and II. The question discussed was whether the forcing apart of the valencies (*a*) and (*b*) of a carbon atom from an inclination of $2\tan^{-1}\sqrt{2}$ to one of $\frac{2}{3}\pi$ radians, which, according to Baeyer's strain theory necessarily accompanies the production of the *cyclo*hexane ring, would cause the other two valencies (*c*) and (*d*) to approach one another. They might, it was suggested, approach one another in such a way as to divide the remaining space into three equal angles as in Fig. (ii A); or, alternatively, they might be quite unaffected by the straining of (*a*) and (*b*) and remain, as Fig. (ii B) shows, at the normal angle of $2\tan^{-1}\sqrt{2}$.

It was pointed out that if the first of these hypotheses, that represented in Fig. (ii A), were correct, and side-chains attached to (*c*) and (*d*) were in closer proximity when (*a*) and (*b*) were bound in a *cyclo*hexane ring than is the case in Fig. (i), where (*a*) and (*b*) are free, then the elimination of groups or elements such as, for example, hydrogen and bromine as hydrogen bromide, from the side-chains of substitution products of *cyclo*hexanediacetic acid should proceed with greater readiness than when corresponding derivatives of dimethylglutaric acid are employed. Further, the ring compounds formed as a result of the elimination might be expected to possess a greater general stability in the former case than in the latter. If, on the other hand, the second alternative,

for which Fig. (ii B) is drawn, is the correct one, there should be no difference in the two cases.

Experimental evidence was, as a matter of fact, clearly in favour of the first hypothesis. Thus, for example, *trans-cyclo*hexane*spiro-cyclo*propane-1:2-dicarboxylic acid, which contains the carbon

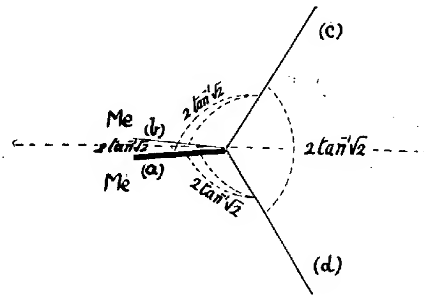


Fig. (i)

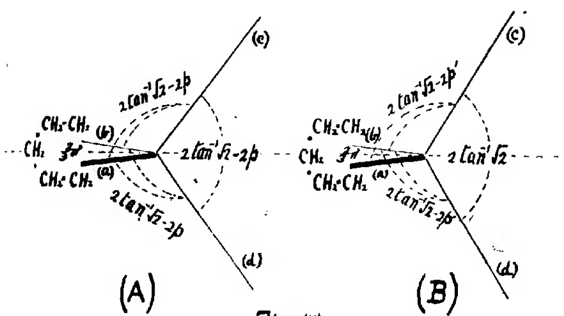


Fig. (ii)

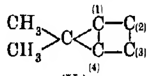
skeleton IV, was found to possess a distinctly greater stability than *trans*-caronic acid represented by the outline III:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{(3)}{C}<\!\!\begin{matrix} C_{(1)} \\ | \\ C_{(2)} \end{matrix} \qquad\qquad CH_2\!\!<\!\!\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!\!>\underset{(3)}{C}<\!\!\begin{matrix} C_{(1)} \\ | \\ C_{(2)} \end{matrix}$$

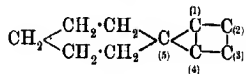
(III.) (IV.)

The present paper extends the comparison to substances of a rather more complex type, which contain a *cyclo*butane ring joined to the

*cyclo*propane ring by two carbon atoms common to both. The structures of these compounds are indicated by the outlines V and VI:



(V.)



(VI.)

It is apparent that the presence of the *cyclo*butane ring in structures V and VI will make a considerable difference in the kind of effect that one might expect to observe. This can best be understood by representing the strained valencies according to a graphical method which depends for its rational basis on the following considerations.

In Fig. (iii), which is drawn to correspond with formula III, the

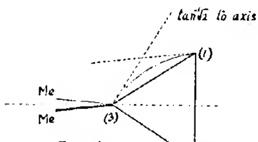


Fig. (iii)
(Cyclopropane ring in plane of paper)

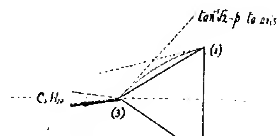


Fig. (iv)
(Cyclopropane ring in plane of paper)

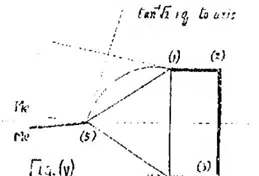


Fig. (v)
(Cyclopropane ring in plane of paper. Cyclobutane ring inclined to paper)

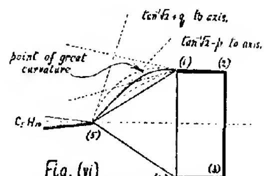


Fig. (vi)
(Cyclopropane ring in plane of paper. Cyclobutane ring inclined to paper)

carbon atoms of the *cyclo*propane ring are represented as points at the corners of an equilateral triangle. Now in the case of such a compound as ethane it can scarcely be doubted that the resultant of the attracting forces which bind the two carbon atoms together, that is to say the valency, is directed along the straight line joining the centres of the carbon atoms. With *cyclo*propane, however, the case is different. For here, according to the strain theory, we have each one of the carbon atoms of the ring reacting on those of its valencies which participate in the ring in such a way as to *tend* to make them emanate from the atom in directions inclined to one another at an angle of $2\tan^{-1}\sqrt{2}$. If the carbon atoms were entirely successful in bringing about this result, then, since two

valencies emanating from the same carbon atom at an angle of $2\tan^{-1}\sqrt{2}$ have to reach the two remaining corners of the equilateral triangle, it is clear that the only way in which they could do so is by describing curved paths. The simplest curve which, in these circumstances, a valency could describe would be the arc of a circle each of the terminal tangents of which makes an angle of $\tan^{-1}\sqrt{2}$ with the median through the corresponding corner of the equilateral triangle. This path is drawn in the case of the valency (3:1) in Fig. (iii). It represents a state in which the carbon atoms would be entirely free from distortion of the kind we are considering, the whole being borne by the valencies; that is to say, the physical stress would reside solely on the inter-atomic medium in which the forces of valency are propagated. The valencies will, however, on their part, tend to reduce their potential energy by shortening their paths, and if *they* completely succeeded would stretch themselves along the straight lines joining the carbon atoms. This would throw the whole of the strain back on the latter, since now the initial directions in which the ring-valencies leave a carbon atom are inclined, not at $2\tan^{-1}\sqrt{2}$, but at $\pi/3$. It is probable, therefore, that an equilibrium of stresses will be set up, and that the valencies will occupy paths which lie between the straight lines and the limiting arcs, the arrangement being of such a kind as to cause part of the strain to be taken up by the distorted carbon atoms and part by the bent valencies.

Experimental support can be claimed for this view. For in Part I. there were recorded experiments which yielded decided evidence that part at least of this kind of strain is actually taken up by the carbon atoms. In particular, it was shown that, when two valencies of a carbon atom are bound in a *cyclo*hexane ring, groups attached to the other two valencies apparently take up an altered relative position. It is obvious that this could never happen if the strains existing in the *cyclo*hexane ring resided solely on the valencies participating in the ring, none at all being borne by the carbon atom which carries the side-chains. Similarly, strains existing in one ring of a *spiro*-compound could not possibly make themselves felt in the second ring unless communicated by a spirane carbon atom, which itself is in a state of strain. According to the experiments described in Part I., such communication of strain across the spirane carbon atom appears actually to take place, and one can only conclude therefrom that the spirane atom itself is by no means in an unstrained condition.

If it be true that part at least of the strain of the *cyclo*hexane ring is actually taken up by the carbon atoms, then regarding the matter from the graphical point of view, we may say that the

valencies of the *cyclo*hexane ring, and presumably of any other alicyclic ring, occupy paths which are distinctly flatter than the limiting arcs the terminal tangents of which meet at the normal angle $2 \tan^{-1}\sqrt{2}$.

On the other hand, it will be shown in the present paper that it is more difficult to close the *cyclo*butane ring in the formation of certain bridged-*spiro*-compounds of the type VI (p. 322) than it is in the formation of corresponding bridged-ring compounds of the type V (p. 322). Further, the former, when obtained, are less stable than the latter in certain specific positions entirely in accord with the views here put forward. If the stresses existing in the *cyclo*hexane ring can be communicated to the *cyclo*butane ring, or to side-chains attached to the *cyclo*propane ring before the *cyclo*butane has been closed, then it follows that the valencies of the *cyclo*propane ring, as well as the spirane carbon atom, must take part in the transmission of stress. With entirely unstrained valencies this is inconceivable, and one is therefore forced to the conclusion that the valencies themselves are strained.

The graphical aspect of this is that the valencies concerned, and therefore probably all ring-bound valencies, must occupy paths which are not straight lines, which are, in fact, distinctly curved. The curvature of such a path will, as we have already seen, be less than that of the limiting arc the terminal tangents of which meet at $2 \tan^{-1}\sqrt{2}$, and the path may therefore be regarded as lying somewhere between a straight line on the one hand and a limiting curve on the other.

Exactly where the position of equilibrium of a particular valency lies, and what the precise shape of its true path is, it is impossible at present to say; but the view that the true equilibrium-path lies somewhere between the rectilinear path, which represents the limiting case in which the valency is unstrained, and the curved path which stands for the other limit in which the whole of the distortion resides on the valency and none at all on the carbon atom, affords a simple, and, so far as it goes, a fairly adequate hypothesis in regard to the facts observed. If we accept the point of view that the more strained a valency is the more prone it is to break, then among the factors which determine the equilibrium of strain-distribution will certainly be found the number of groups attached to the carbon atoms concerned; for the tendency which ring compounds have to undergo fission between quaternary carbon atoms is well known. The electrochemical character of the substituents will, of course, be another determining factor.

Thus it would seem that there are three causes affecting the

stability of any valency which participates in a fully reduced alicyclic structure:

(1) The number of carbon atoms in the ring,

(2) The character and mode of attachment of any attached rings, and

(3) The number, distribution, and character of the substituent groups.

In regard to the first of these causes Baeyer's simple conception has had a very great degree of success in explaining the broad facts; so much so that one cannot but accept it as an approximation to the truth. In its elemental form, however, it does not consider the question as to whether the atoms or the valencies are the seat of the postulated strain, and, consequently, is not in a position to take into account the mode of operation of causes (2) and (3), which present us with two unsolved problems. The series of which this paper is Part II. is an attack on the former of these. In regard to the latter all that can at the moment be said is that the present considerations lead to the view that whilst causes (1) and (2) determine the maximal strain or curvature which any particular valency can be called on to bear, cause (3) operates in such a way as to settle exactly what fraction of that maximum it shall bear.

The uncertainty which surrounds the operation of cause (3) constitutes a difficulty which one meets with in planning experiments with a view to study the mode of action of cause (2). If, however, one is careful only to compare substances in which similar, and similarly situated, substituent groups are present, the strain on a valency may fairly be taken to be measured by the greatest strain which that valency could be called on to bear in the limiting equilibrium. It will actually, of course, be just a fraction of this, but if the groups are alike it will be the same fraction for all the substances. In such cases, therefore, the strain existing on a valency is, from the graphical point of view, measured by the degree of curvature of the limiting curved path.

Fig. (iii), p. 322, is an application of this method to the *cyclo*propane ring structure III (p. 321), and has already been mentioned. The limiting curve for the valency (3:1) is drawn. Its terminal tangents make angles of $\tan^{-1}\sqrt{2}$ with the corresponding medians, and its curvature, taking the side of the triangle as unity, is $\sqrt{2}-\frac{1}{3}\sqrt{3}$.

Applying the same method to the *cyclo*hexane-*spirocyclo*propane structure IV (p. 321) we obtain Fig. (iv) (p. 322), in which, for reasons referred to at the beginning of this paper and given in detail in Part I., the terminal tangents of the limiting curve of the

valency (3:1) are drawn to make angles with the corresponding medians less than the normal value $\tan^{-1}\sqrt{2}$ by, say, p radians. The curvature of this curve is less than that of the curve in Fig. (iii) by about $\frac{1}{6}(7-2\sqrt{6})p$, a figure which may be taken as a measure of the increase in stability of the bond (3:1) which was proved experimentally in Part I.

The structure V (p. 322) is interesting as exhibiting a difference in exactly the opposite sense. The fact that two of the valencies of the carbon atom (1) are held in a *cyclo*butane ring will, according to the views put forward in Part I., tend to make the initial directions in which the other two valencies leave the carbon atom spread out in such a way as to form angles with one another and with the *cyclo*-butane-ring-bound valencies greater than would be the case if the *cyclo*butane ring had not been closed. This will involve an increase in the initial divergence of the valencies (1:4) and (1:5). The limiting arc between the carbon atoms (5) and (1) is therefore drawn (Fig. v, p. 322) to suit terminal tangents inclined to the corresponding medians at angles which are greater than $\tan^{-1}\sqrt{2}$ by, say, q radians. The curvature is therefore greater than $\sqrt{2}-\frac{1}{3}\sqrt{3}$ by about $\frac{1}{6}(7-2\sqrt{6})q$.

The point of present interest is, of course, to see how a bridged-ring compound of the type V compares with a bridged-*spiro*-compound of the type VI (p. 322). It will be observed that in the latter case the limiting curve for the valency (5:1) cannot possibly be symmetrical. For whilst the carbon atom (5) is, on account of the *cyclo*hexane ring, tending to reduce the angle which the terminal direction of the curve makes with the median to the value $\tan^{-1}\sqrt{2}-p$ radians, the carbon atom (1), as a result of its being involved in the *cyclo*butane ring, is endeavouring to enhance the corresponding angle at that end of the curve to $\tan^{-1}\sqrt{2}+q$ radians. The true curve, therefore, will lie between the dotted arcs of curvatures $\sqrt{2}-\frac{1}{3}\sqrt{3}-p/6(7-2\sqrt{6})$ and

$$\sqrt{2}-\frac{1}{3}\sqrt{3}+q/6(7-2\sqrt{6}),$$

approximating to the inner arc near the carbon atom (5), and to the outer near the carbon atom (1). Such a path, it is clear from Fig. (vi) (p. 322), must contain a region of comparatively great curvature, and we may therefore expect the bond (5:1) in bridged-*spiro*-compounds of the type VI (p. 322) to be noticeably less stable than the same bond in corresponding compounds of the bridged-ring series V.

The effect just noticed will, of course, be by far the greatest which the *cyclo*hexane ring could be expected to have on the attached dicyclic system. The reactions on the bonds (1:2) and (1:4) will

be next in importance, but of the second order. It is, however, of interest briefly to examine them. The fact that the limiting curve of the valency (5:1) is, on the whole, depressed below the arc which corresponds with the limiting curve of the same valency in Fig. (v) necessitates that the true path of the same valency in Fig. (vi) is, even near the carbon atom (1), rather less divergent from the rectilinear path than is the case in Fig. (v). This will involve a small effect on the valency (1:2) in the direction of an increase in the curvature of its limiting curve. The bond (1:2) should therefore be slightly more strained and less stable in the series VI than in the series V.

The effect of the strains in the *cyclo*hexane ring on the bridge-bond (1:4) is also of the second order, the depression of the bond (5:1) being the determining factor. In this case the fact that the bonds (1:5), (1:4), and (1:2) have their curves in different planes makes the geometrical construction more complicated. It would appear, however, that the effect should be in the direction of a decrease of stability, although, of course, a very slight one.

There remains for consideration the bond (2:3). The effect in this case will be still smaller, of the third order in fact, and probably beyond the limits of detection. It should be in the direction of an increase in stability.

It may be stated here that the results of the experiments described in this paper are in the most complete accord with all the above conclusions.

The most striking fact which emerged during the experimental study was the marked decrease in the stability of the bond (5:1), of compounds of the type VI, when compared with corresponding substances of the type V (see sections C, D, and G). The fission of this bond was brought about with great ease in certain substances of the former type by alkaline reagents which appeared to be without effect on the latter. This is in agreement with the first of the main conclusions reached as a result of the conception of flexible valencies. The agreement is particularly interesting in this case, for whereas in the comparison of the *cyclo*propane derivatives of types III and IV (p. 321) carried out in Part I. it was found, in agreement with the requirements of theory, that the *cyclo*hexane ring had a stabilising influence, in the bridged series V and VI the hypothesis leads us to anticipate exactly the reverse.

Definite experimental evidence (section B) was also obtained on the effect on the bond (1:2) of the presence of the *cyclo*hexane ring in the *spiro*-compounds. The expected effect is in the nature of an increase in strain, that is, a decrease in stability, and is small in magnitude. Actually we were not able to find a reagent which

would break this bond in a compound of the type VI (p. 322), and would not also break the same bond in one of the type V. This was, at any rate, in part, due to the fact that it did not appear to be possible to break the bond (1:2) in the series VI without first breaking the less stable bond (5:1). This, so far as it goes, is valuable, as it indicates that the effect of the *cyclo*hexane ring on the bond (1:2) is of a smaller order than the effect on the bond (5:1). Fortunately, there is, however, a more precise and more delicate method of experiment. The *cyclo*hexane*spiro*di*cyclo*pentane structure VI was, in our experiments obtained from *cyclo*hexane-1:1-diacetic acid by a method which involved first the closing of the *cyclo*propane ring, and then of the *cyclo*butane ring, by the establishment of the bond (3:4). Now the additional instability which we have been led to expect the bond (1:2) in the *spiro*-structure VI to exhibit is due to the tendency which there is, owing to the *cyclo*hexane ring, for the angle between the bonds (1:4) and (1:5) to increase. It is obvious that this tendency will have greater effect if the bond (3:4) has not been established than would be the case if it had, for in the former case the tendency will not be resisted by the strained bonds of the *cyclo*butane ring. The result will be to magnify the effect by drawing further apart the carbon atoms (3) and (4) to an extent which might quite well be sufficiently great to make it appreciably more difficult to close the *cyclo*butane ring in the series VI than in the series V. A set of comparative experiments, made in order to discover whether such an effect could be detected, revealed its existence very clearly. The interest of these experiments lies in the fact that they show that the stresses in the *cyclo*hexane ring have been communicated to the bond (1:2), a phenomenon which would seem necessarily to involve the assumption that the bond (5:1), as well as the carbon atoms (5) and (1), are in a state of strain.

With regard to the bond (1:4) in the structures V and VI (p. 322) there is available quite a good method of experiment, since sodium amalgam readily breaks this bond in certain substances belonging to these types without attacking in the slightest degree any of the other bonds in the molecules (see section E). The reductions occupy several hours, and can readily be conducted at constant temperature and under comparable conditions. By making comparative experiments along these lines it was discovered that, although the reactions proceeded in much the same way in the two cases, there was a considerable difference in the reaction velocities, the reductions proceeding more rapidly in the bridged-*spiro*-series VI than in the bridged-ring-series V. This is in agreement with the conclusions already reached on theoretical grounds (p. 327), but it

has also some interest from another point of view. It might be thought possible that valencies are so extremely elastic as to be capable of stretching as well as of bending. If that be so, the valency (1:4) ought to be less stretched out in the structure VI, in which the *cyclo*hexane ring is tending to reduce the angle at which the bonds (5:1) and (5:4) emerge from the spirane carbon atom (5), than in the structure V, which contains no *cyclo*hexane ring. Any such difference in the degree of elongation of the bond (1:4) ought to manifest itself as a marked difference of stability, since the forces between two carbon atoms must vary as some power, probably a high power, of the distance between them. As a matter of fact, the difference of stability which the reduction experiments reveal is in precisely the opposite sense from that which this view requires. This appears to us to show that no appreciable lengthening occurs, and that probably all carbon-to-carbon valencies have the same fixed length. It may also be noticed that the effect observed is the opposite to what would be expected if the bonds occupied inflexible straight lines. For in this case the tendency which the *cyclo*hexane ring has to reduce the angle between the bonds (5:1) and (5:4) (compare Part I.) should operate in such a way as to increase the stability of the bond (1:4). These facts, therefore, constitute a strong argument in support of the conception of flexible valencies.

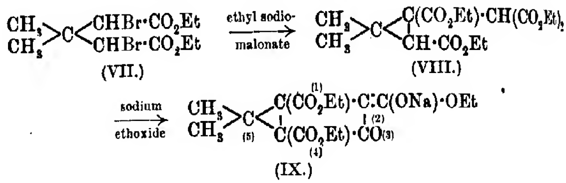
There remains to be mentioned finally a set of experiments which were undertaken in order to obtain information regarding the bond (2:3). This bond, according to the conclusions expressed on p. 327, should be practically unaffected by the strains in the *cyclo*hexane ring. Actually we were not successful in finding a reagent which would attack this bond in a compound of the type VI, even when the stability of the bond was reduced by the introduction of an alkyl group at the carbon atom (2), without first attacking one of the *cyclo*propane bonds adjacent to the spirane carbon atom. However, the experiments were interesting as confirming our previous experiences regarding the instability of these bonds, and were in harmony with the conclusions already reached in regard to the insignificance of the effect which the *cyclo*hexane should have on the bond (2:3).

In order to avoid confusion in what follows it ought perhaps to be pointed out that the bonds (5:1) and (5:4) are equivalent in the carbon skeletons V and VI (p. 322), and only become dissimilar when substituent groups are introduced unsymmetrically. This is actually the case with the compounds with which we have experimented, and it so happens that the bond split in all the substances which were subjected to fission by alkalis is, according to the method

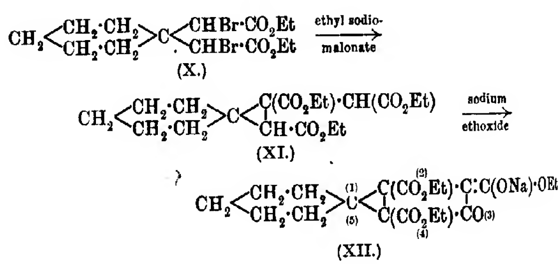
of numbering employed throughout, the bond (5:4), not the bond (5:1). This, it is clear, invalidates nothing, and, in fact, the agreement would be formal as well as actual if in the formulæ which follow we had numbered the di*cyclo*pentane ring the other way round. The objection to doing this is that one would then meet with the same lack of formal consistency in regard to the bonds (1:2) and (3:4).

(B) *Formation of the Bridged-ring Systems V and VI* (p. 322): *Closing of the* cyclo*Butane Bond* (3:4).

Some time ago, in a paper published by one of us in conjunction with W. H. Perkin (T., 1901, **79**, 729), it was shown that when the dibromo-ester of $\beta\beta$-dimethylglutaric acid (VII) was treated with ethyl malonate and sodium ethoxide, condensation took place in two stages, the ultimate product being an insoluble, yellow sodium derivative of ethyl dimethyldi*cyclo*pentanonetricarboxylate (IX). It was



therefore to be expected that if *cyclo*hexane-1:1-diacetic acid were used in place of dimethylglutaric acid a similar condensation would ensue:



The sodium derivatives IX and XII clearly belong respectively to the types V and VI (p. 322), and it was therefore decided to make their formation and decompositions subjects of comparison.

It was found possible to prepare the sodium *spiro*-compound (XII) direct from ethyl dibromo*cyclo*hexanediacetate (X) and ethyl

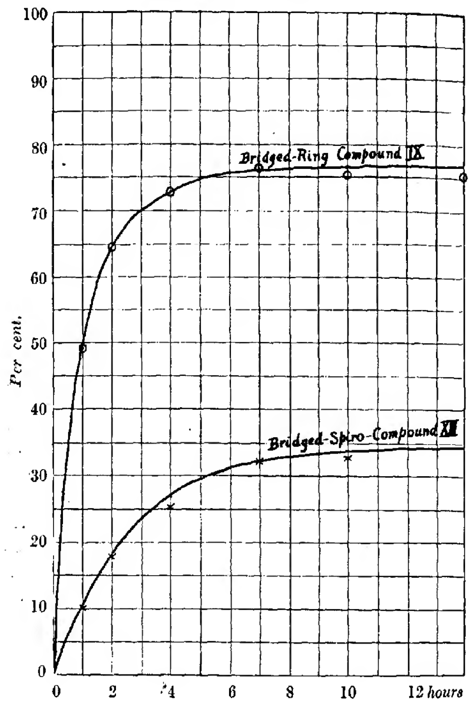
sodiomalonate under the same conditions as are employed in preparing the sodium ring compound (IX) from ethyl dibromodimethylglutarate (VII). Direct comparison of the two condensations is, however, complicated by the fact that, whilst ethyl dibromodimethylglutarate (VII) can readily be obtained in a state of purity by distillation, the corresponding *cyclo*hexane derivative (X) decomposes when distilled. We were therefore forced to use a crude bromination product containing only 76—80 per cent. of the dibromo-ester. Nevertheless, the difference between the two cases is significant. Two experiments, one with the bromo-ester of dimethylglutaric acid, and the other with the bromo-ester of *cyclo*hexanediacetic acid, carried out under comparable conditions (except that sufficient excess of the crude *cyclo*hexane ester to allow for the impurities was used), gave in the first case a 62 per cent. yield of the sodium compound (IX, p. 330), and in the second a 13 per cent. yield of the sodium *spiro*-compound (XII, p. 330).

In order to make the comparison more definite, the tetraethyl ester XI (p. 330) was prepared in a state of purity. The internal condensations of the esters VIII and XI (p. 330) with alcoholic sodium ethoxide, whereby alcohol is eliminated and the bridged structure formed, were then carried out in a series of experiments made under comparable conditions. Several pairs of parallel experiments were made, in which the two esters were boiled with alcoholic sodium ethoxide under standard conditions for different lengths of time, at the end of which the insoluble sodium compounds were collected and weighed. The results are given in the experimental part of this paper (p. 359). The figures for the yields in the two cases lie upon fairly smooth but widely divergent curves (Fig. vii). These curves clearly show that the velocity of formation of the bridged-ring structure is much greater than the velocity of formation of the *spiro*-compound. The times required for a 20 per cent. conversion are in the ratio of approximately 10 to 1. An examination of the curves shows that, if x is the yield (per cent.) and t the time, the quantity $-\partial/\partial x(dx/dt)$ is almost invariable with time and has a definite positive value for each curve, being about $0{\cdot}97^{-1}$ hours for the bridged-ring compound and about $0{\cdot}33^{-1}$ hour for the bridged-*spiro*-derivative. The velocity constants for the formation of the sodium compounds are therefore approximately in the ratio of 3 to 1. The best yields obtainable in the two cases are 77 per cent. and 38 per cent. respectively, but a longer time is necessary to produce a 38 per cent. yield of the *spiro*-compound than is required to obtain a 77 per cent. yield of the ring compound. The fact appears to be that the *spiro*-ester XI (p. 330) will only condense with itself when present in the sodium ethoxide

in considerable concentration. For, whereas under the experimental conditions which give the best yield (77 per cent.) of the sodio-ester, IX, the tetraethyl ester, VIII (p. 330), almost entirely disappears from the reaction mixture, when the ester XI is treated so as to produce a maximal yield of the sodio-*spiro*-ester (38 per cent.), then,

FIG. (vii).

Establishment of the bond 3 : 4.



although longer time is allowed in this case, the conversion is found to be only partial, about 15 per cent. of the tetraethyl ester being recoverable. Yet prolonging the time of reaction does not appear appreciably to increase the yield of sodium compound or reduce the quantity of tetraethyl ester recovered.

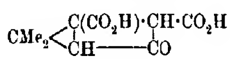
These experiments clearly show that it is more difficult to estab-

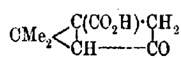
lish the bond (3:4) of the *cyclo*butane ring to form the *spiro*-compound XII than it is in the formation of the ring compound IX. Indeed, the low yield of the former compound was one of the greatest practical difficulties of the research.

(C) *Hydrolytic Decompositions of the Bridged-Ring Derivatives IX and XII* (p. 330): *Stability of the* cyclo*Propane Bond* (4:5).

The first evidence of a difference of stability between compounds of the bridged-*spiro*-series VI and those of the bridged-ring series V (p. 322) was obtained in the course of some experiments on the hydrolysis of the sodium *spiro*-compound XII (p. 330).

The effect of hydrolysing agents on the sodium compound IX has already been described in the paper with W. H. Perkin (*loc. cit.*), and the general conclusion reached was that the end-product of the action of alcoholic potassium hydroxide was a mixture of the dibasic and monobasic acids XIII and XIV, and that the same two acids

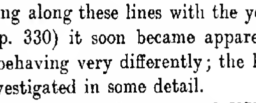

(XIII.)


(XIV.)

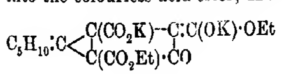
were formed by the action of dilute sulphuric acid. The dibasic acid XIII when heated with water in a sealed tube was found to yield the monobasic acid XIV.

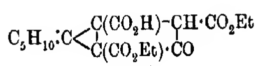
On experimenting along these lines with the yellow sodium *spiro*-compound XII (p. 330) it soon became apparent that the *spiro*-compounds were behaving very differently; the hydrolytic products were therefore investigated in some detail.

When the yellow sodium *spiro*-compound XII was treated with cold dilute acid a colourless, solid ester, $C_{19}H_{26}O_7$ (XV), was pro-


(XV.)

duced. This ester could be transformed by cold alcoholic potassium hydroxide into the yellow potassium salt, XVI, and thence by acids into the colourless acid-ester, XVII.


(XVI.)


(XVII.)

Regarding the question as to which of the three carbethoxyl groups has been attacked by the reagent, it is clear that it cannot be that attached to the carbon atom (2); for if it were, the forma-

tion of a yellow, insoluble potassio-compound so very similar to the original sodium compound would be exceedingly improbable. The fact that it is the 1-carbethoxyl group, and not the 4-carbethoxyl, which has been attacked follows from the production by further hydrolysis of the acid-esters XVIII and XXI, about the constitution of which no doubt exists.

The first product of the action of boiling alcoholic potassium hydroxide on either of the compounds XVI or XVII was a colourless, very readily soluble potassium salt of the ethyl dihydrogen ester XVIII:

$$C_5H_{10}{:}C{<}\begin{array}{l}C(CO_2H)\text{—}CH\cdot CO_2H\\ C(CO_2Et)\cdot CO\end{array}$$

(XVIII.)

The constitution of the acid-ester XVIII follows from the fact that it is obviously formed by the hydrolysis of the metal-substituted carbethoxyl group in the yellow potassium compound of the diethyl hydrogen ester. The other possible formula (XIX) of the diethyl hydrogen ester would give an ethyl dihydrogen ester of the constitution XX. The formula XX was, however, easily shown to

$$C_5H_{10}{:}C{<}\begin{array}{l}C(CO_2Et)\cdot CH\cdot CO_2Et\\ C(CO_2H)\text{—}CO\end{array} \qquad C_5H_{10}{:}C{<}\begin{array}{l}C(CO_2Et)\cdot CH\cdot CO_2H\\ C(CO_2H)\text{—}CO\end{array}$$

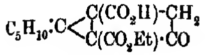
(XIX.) (XX).

be incorrect by an experiment on the effect of treating the substance with acetyl chloride. With this reagent it readily yielded an anhydride, which, on treatment with water, furnished the original acid-ester. These facts clearly favour formula XVIII, in which the free carboxyl groups are attached to contiguous carbon atoms, and rules out the alternative formula XX. We must also regard XVII as the true formula of the diethyl hydrogen ester, since a substance of the formula XIX could not possibly yield the ethyl dihydrogen ester XVIII.

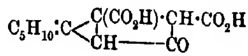
The acid-ester XVIII can also be produced from the triethyl ester XV (p. 333) by hydrolysis with hydrochloric acid. Indeed, up to this point hydrolysis with alcoholic potassium hydroxide and with hydrochloric acid proceeds along the same lines. The first product of the action of boiling hydrochloric acid on the ester XV is the diethyl hydrogen ester XVII (p. 333), which, by continued action of the same reagent, is converted into the ethyl dihydrogen ester XVIII (above).

The further action of hydrochloric acid causes the substance to decompose simultaneously in two ways, losing, in the one case, a carboxyl group, and in the other a carbethoxyl group. The groups eliminated will, of course, be those in the positions (2) and (4) con-

tiguous to the carbonyl group, and the products must therefore possess the constitutions XXI and XXII:



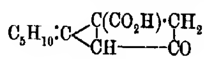
(XXI.)



(XXII.)

These formulæ are in complete accord with the properties of the substances. The acid-ester XXI, for example, melted without decomposition and gave no coloration with ferric chloride, showing that the free carboxyl group is not adjacent to the carbonyl group, and that the carboxyl group which was attached to the carbon atom (2) in the acid-ester XVIII has been removed. The dibasic acid XXII, on the other hand, melted with decomposition, gave a crimson colour with ferric chloride, and when treated with acetyl chloride gave an anhydride from which the original acid could be regenerated by treating with water. These facts clearly establish formula XXII.

The formation side by side of the acids XXI and XXII does not constitute quite the final stage of the hydrolysis by hydrochloric acid of the ethyl dihydrogen ester XVIII (p. 334). For the acid-ester XXI on prolonged boiling with hydrochloric acid loses its 4-carbethoxyl group, yielding the monocarboxylic acid, XXIII:



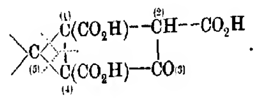
(XXIII.)

The dibasic acid XXII, on the other hand, was not changed appreciably even on boiling for eighty-seven hours with hydrochloric acid. The final product of the action of this reagent on the acid-ester XVIII was therefore a mixture of the dibasic acid and the monobasic acid (XXII and XXIII).

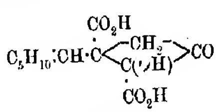
Further, the dibasic acid XXII was readily converted into the monobasic acid XXIII by heating for a few minutes at 200° with water. All the acid-esters (XVII, XVIII, and XXI) of the series reacted at this temperature with water, giving the same monobasic acid, usually in very good yield. The neutral triethyl ester XV (p. 333), however, required the presence of a trace of an acid, such as acetic or hydrochloric acid, in the water. The presence of a small quantity of butyric acid even was found to be quite sufficient, so that in the cases of the acid-esters the reaction is in all probability autocatalytic, the catalyst being the hydrogen ions produced initially by the electrolytic dissociation of the acid-esters themselves, and in the later stages of the reaction by the dissociation of the monocarboxylic acid XXIII or of carbonic acid. In the case of the

triethyl ester it is necessary artificially to introduce some hydrogen ions in order to start the reaction.

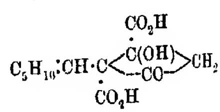
Alkaline hydrolysis of the acid-ester XVIII (p. 334) proceeded in quite a different direction, the product being an acid of the formula $C_{12}H_{16}O_6$. This substance is a dibasic acid. It is not an aldehyde, and contains no lactone ring. It is therefore a fission product formed by the breaking of one of the bonds (1 : 2), (1 : 4), (1 : 5), or (4 : 5) of the dicyclic system:



One of the three carboxyl groups originally present in the molecule has been lost, and, since the substance gives no colour reaction with ferric chloride, it is to be presumed that it is the carboxyl group attached to the carbon atom (2) which has disappeared. The question as to which of the four possible bonds has been broken is settled very clearly by the properties of the substance. Thus fission of the *cyclo*butane ring at the bond (1 : 2) should yield either a derivative containing an open-chain acetoacetic acid residue or a hydroxy-compound capable of forming a γ-lactone, according to the way in which the elements of water are added to the molecule at the point of fission. The substance actually obtained was found to be remarkably stable towards boiling alkalis and showed no tendency to pass into a lactone. On the other hand, although a *trans*-acid, it forms an anhydride with the greatest ease. For this reason it may be safely assumed that the 1- and the 4-carboxyl groups are attached to contiguous carbon atoms, and that the bridge-bond (1 : 4) has remained intact. The bond which has been broken is therefore one of the *cyclo*propane bonds (1 : 5) and (4 : 5), and since the substance is not a γ-hydroxy-acid, it must have one of the two following formulæ:



(XXIV.)



(XXV.)

Although both these formulæ are in harmony with the properties of the substance, there can be little doubt that formula XXIV, and not formula XXV, is correct for this reason: The monobasic acid XXIII (p. 335) does not undergo fission with alcoholic potassium hydroxide. The fission therefore seems to be connected with tl

quaternary carbon atom in the position (4). If this be so it is reasonable to assume that splitting takes place at a point adjacent to this carbon atom. An indirect but interesting confirmation of this conclusion will subsequently be referred to (p, 345).

The substance to which the formula XXIV has been assigned separates from water with two molecules of water of crystallisation. The anhydrous compound when heated at 250° was found to pass into an anhydride which gave with water a new dibasic acid, also of the composition $C_{12}H_{16}O_6$. This did not take up water of crystallisation and melted with the immediate elimination of water-vapour. On boiling with hydrochloric acid, it was quantitatively converted into the isomeride previously mentioned. These relationships clearly indicate that geometrical isomerism of the *cis-trans*-type is here being encountered, both the acids $C_{12}H_{16}O_6$ having the structure represented by the formula XXIV, which clearly requires the existence of this kind of isomerism.

The relationships between the various substances obtained by the hydrolysis of ethyl *cyclo*hexane*spiro*di*cyclo*pentanonetricarboxylate and of its sodium derivative are collected together for convenience in table I.

In order to study more closely the contrast presented by the hydrolytic reactions in the dimethyldi*cyclo*pentane and the *cyclo*hexane*spiro*di*cyclo*pentane series, a number of direct comparative experiments were made in order to determine the relative speeds at which the acid-esters of the two types decomposed in the presence of alkali. The substances chosen were the ethyl dihydrogen ester, XXVI,* and the analogous substance in the bridged-

$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>C<\!\!\begin{array}{l} C(CO_2H)\text{-}CH\cdot CO_2H \\ C(CO_2Et)\cdot CO \end{array}$$

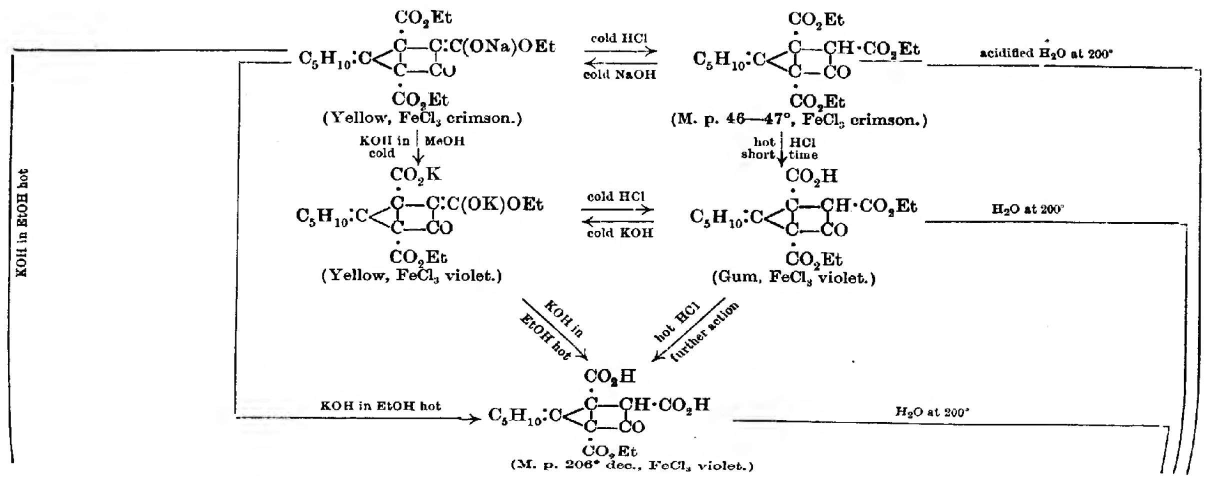
(XXVI.)

spiro-series, namely, the acid-ester XVIII (p. 334). The bridged-ring ester XXVI decomposes under the prolonged action of boiling alcoholic potassium hydroxide, yielding the monobasic acid XIV (p. 333). The bridged-*spiro*-ester XVIII, on the other hand, undergoes fission with the same reagent, giving the *cyclo*hexyl-*cyclo*butane acid XXIV (p. 336).

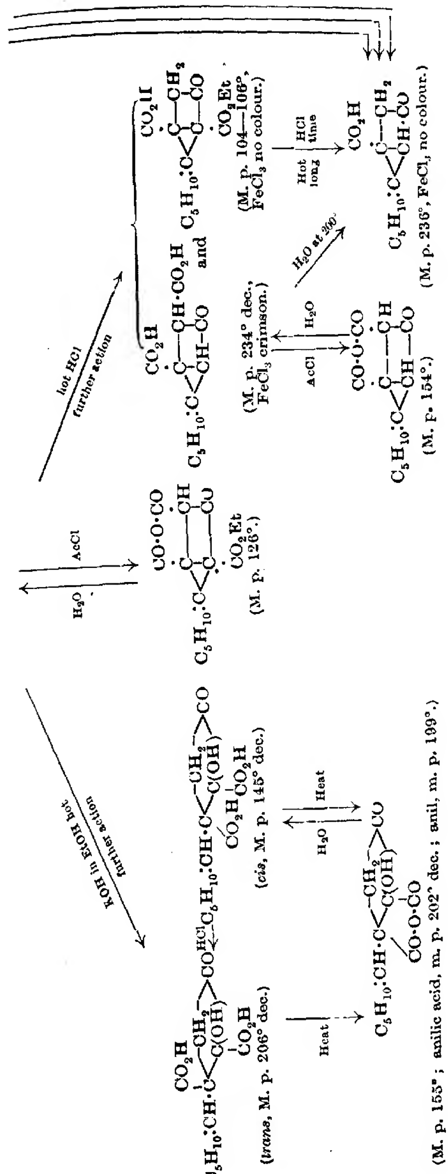
There is, however, a remarkable difference in the ease with which the two reactions proceed. Thus in one pair of parallel experiments made under comparable conditions, the acid-ester XVIII of the bridged-*spiro*-series gave an 85 per cent. yield of the fission

* This substance was not isolated during the earlier research. Its properties and mode of formation are therefore given in a note at the end of the experimental part of this paper.

Table I



CO_2Et
$C_5H_{10}:C<$ C—C:C(ONa)OEt, C—CO
CO_2Et
(Yellow, $FeCl_3$ crimson.)
cold HCl
cold NaOH
CO_2Et
$C_5H_{10}:C<$ C—CH·CO_2Et, C—CO
CO_2Et
(M. p. 46—47°, $FeCl_3$ crimson.)
acidified H_2O at 200°
KOH in MeOH cold
CO_2K
$C_5H_{10}:C<$ C—C:C(OK)OEt, C—CO
CO_2Et
(Yellow, $FeCl_3$ violet.)
cold HCl
cold KOH
hot HCl short time
CO_2H
$C_5H_{10}:C<$ C—CH·CO_2Et, C—CO
CO_2Et
(Gum, $FeCl_3$ violet.)
H_2O at 200°
KOH in EtOH hot
KOH in EtOH hot
hot HCl further action
KOH in EtOH hot
CO_2H
$C_5H_{10}:C<$ C—CH·CO_2H, C—CO
CO_2Et
(M. p. 206° dec., $FeCl_3$ violet.)
H_2O at 200°



product, whilst, on the contrary, the bridged-ring acid-ester XXVI was recovered unchanged to the extent of 93 per cent., only a trace of the monocarboxylic acid being isolated. No fission product of the dimethyldi*cyclo*pentane series was isolated in the course of these experiments.

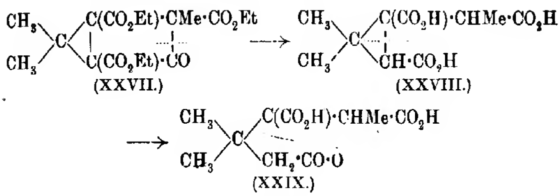
These experimental comparisons are interesting as showing the extraordinary facility with which the bond (4:5) in the bridged-*spiro*-series is broken. They have, however, interest from another point of view. For if they had not been made it would have been possible to advance an explanation of the difference in the ease of fission of the bond (4:5) in the two series, based, not on the strain effects of the *cyclo*hexane ring, but on steric hindrance caused by the attached groups. It has already been noticed that it appears to be necessary to have a quaternary carbon atom in the position (4) in order to bring about the fission of the bond (4:5) by alkalis. One might assert, therefore, that in the bridged-*spiro*-series the C_5H_{10}: group attached to the carbon atom (5) has the effect of preventing the elimination of the 4-carbethoxyl group. The carbon atoms (4) and (5), therefore, both remain quaternary in the presence of the alkaline reagent, and splitting occurs between them. One would have to assume, of course, that, although the steric effect of the C_5H_{10}: group attached to the carbon atom (5) is sufficiently powerful to prevent the attack of the reagent on the 4-carbethoxyl group, yet, for some reason unknown, it does not inhibit the attack of the same reagent on the bond (4:5). In the bridged-ring series, on the contrary, the $(CH_3)_2$: group attached to the carbon atom (5) might not have any appreciable steric effect. Splitting, therefore, might not take place in this case owing to the fact that when the acid-ester XXVI (p. 337) is treated with alcoholic potassium hydroxide, the 4-carbethoxyl group is so quickly eliminated that the carbon atom (4) becomes tertiary before the reagent has had time to react appreciably on the bond (4:5).

We were of the opinion at one time that there might be some truth in this way of explaining the phenomena, and it was the desire to test this hypothesis that furnished our chief motive for undertaking the comparative experiments with the acid-esters XXVI and XVIII. It will be seen, however, that the experiments effectively dispose of this explanation, since they show that the 4-carbethoxyl of the acid-ester XXVI is not at all readily eliminated under the experimental conditions employed. We consider this to be strong evidence that the bond (4:5) in the bridged-*spiro*-series is actually under considerable strain, much more so than in the bridged-ring series, and that the fission reactions are not to be accounted for as secondary phenomena due to

steric hindrance or other such causes. Several other examples of the splitting of the bond (4:5) in the bridged-*spiro*-series will subsequently be given (sections D and G).

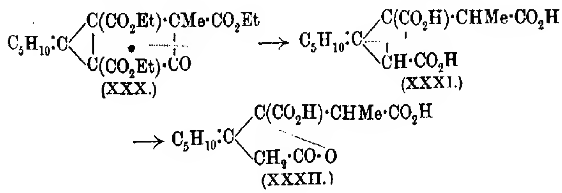
(D) *Hydrolytic Decompositions of the Methylation Products of the Bridged-ring Derivatives IX and XII* (p. 330)*: Stability of the* cyclo*Propane Bond* (4:5) *and of the* cyclo*Butane Bond* (2:3).

In the paper on bridged-ring derivatives, to which reference has already been made, interesting results were obtained by methylating the yellow sodium compound IX (p. 330) and subjecting the methyl derivative to alkaline hydrolysis. It was found that the entrance of the methyl group at the carbon atom (2) in XXVII created a point of instability between the carbon atoms (2) and (3), and that fission took place with the formation, apparently, of the *cyclo*propane acid XXVIII, which then underwent a second fission, giving the dibasic lactonic acid XXIX.


(XXVII.) (XXVIII.) (XXIX.)

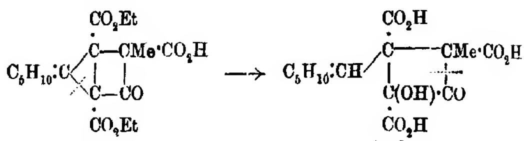
The sodium *spiro*-compound was quite readily methylated by means of methyl iodide. When the ester thus obtained was treated with alcoholic potassium hydroxide, the principal product was a dibasic lactonic acid, evidently a double-fission product, which, however, did not appear to be constituted analogously to the lactonic acid XXIX.

It would appear that there are two quite probable ways in which hydrolytic action might proceed. In the first place, the attack on the ester XXX might commence at the bond adjacent to the

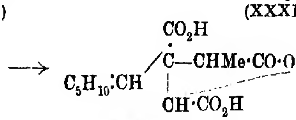

(XXX.) (XXXI.) (XXXII.)

methylated residue and give as the first product a *spirocyclo*propane acid XXXI, which is similar to XXVIII, and would ultimately yield a lactonic acid XXXII strictly analogous to XXIX.

On the other hand, we know that the *cyclo*propane bond (4:5) is a very vulnerable point in the molecule of the unmethylated ester XV (p. 333), and it can scarcely be supposed that the entrance of a methyl group at the carbon atom (2) would stabilise it to any marked degree. If, in spite of the weakening of the bond (2:3) by the methyl group, the bond (4:5) still remains the most readily attacked part of the molecule, we should expect from the behaviour of the unmethylated ester to obtain a *cyclo*hexyl*cyclo*butane acid XXXIII, which would then split again, this time across the bond beside the methylated residue, giving ultimately a dibasic lactonic acid of the formula XXXIV.



(XXX.) (XXXIII.)



(XXXIV.)

In seeking evidence to enable us to decide between the formulæ XXXII and XXXIV, we made a study of the conditions of anhydride formation of the substance. It will be noticed that both formulæ represent substances which, as they have carboxyl groups attached to contiguous carbon atoms, ought easily to form anhydrides. A substance of the formula XXXII would, however, belong to the type of *aa'*-dimethylsuccinic acid, which yields two stereoisomeric anhydrides corresponding with the two stereoisomeric acids (Bone and Perkin, T., 1896, **69**, 266). The *trans*-acid on treatment with acetyl chloride gives a *trans*-anhydride, which on distillation passes into the anhydride of the *cis*-acid, as shown in Scheme 1.

$$trans\text{-Acid} \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} trans\text{-anhydride} \xrightarrow{\text{Heat}} cis\text{-anhydride} \underset{-H_2O}{\overset{+H_2O}{\rightleftarrows}} cis\text{-acid.}$$

Scheme 1.

The lactonic acid XXIX (p. 341), to which XXXII is strictly analogous, actually does form two anhydrides related to one

another and to their acids in this way. Consequently, a substance of the formula XXXII should do the same.

On the other hand, in formula XXXIV, the bond uniting the two carboxyl-bearing carbon atoms forms part of a ring, and hence such a substance would be expected to dehydrate in the manner customary with carboxylated alicyclic compounds, the *trans*-acid, in which the carboxyl groups are on opposite sides of the ring, being incapable of forming its own anhydride, but passing on dehydration directly into the anhydride of the *cis*-acid, as indicated in Scheme 2.

$$trans\text{-Acid} \xrightarrow{-H_2O} cis\text{-anhydride} \underset{-H_2O}{\overset{+H_2O}{\rightleftarrows}} cis\text{-acid.}$$

Scheme 2.

Experiment showed that the lactonic acid obtained by the hydrolysis of the ester XXX (p. 342) actually dehydrated in accordance with Scheme 2. The original product of hydrolysis was the *trans*-acid. It did not eliminate water at the melting point, but was readily dehydrated by acetyl chloride. The anhydride formed was the same substance whether the product of dehydration was distilled or not, and on treatment with water yielded the *cis*-acid. This substance melted, with the immediate elimination of water vapour, and was instantly dehydrated by acetyl chloride. These facts point most distinctly to formula XXXIV (p. 342) as representing the true structure of the stereoisomeric acids.

It is obvious, however, that we have by no means exhausted all the possible formulæ in the above considerations, since either of the intermediate compounds XXXI and XXXIII (pp. 341, 342) could split and take up water in a variety of ways. Indeed, besides XXXI and XXXIII, there are a number of other formulæ which the single-fission product might have. When, however, all these possibilities are examined, it would appear that there are only two formulæ besides XXXII and XXXIV (pp. 341, 342) which fulfil the following conditions relating to the *trans*-lactonic acid isolated:

(*a*) That it is a dibasic lactonic acid of the composition $C_{13}H_{18}O_6$, forming in neutral solution a silver salt, $C_{13}H_{16}O_6Ag_2$, and in alkaline solution a barium salt, $(C_{13}H_{17}O_7)_2Ba_3$.

(*b*) That its free carboxyl groups are attached to contiguous carbon atoms. We regard the behaviour of the substance on dehydration as a proof of this.

(*c*) That it is a γ-lactone. Experiment showed that there was an exceedingly strong tendency for the lactone ring to be formed, and in spite of many attempts we were unable to prepare the free hydroxy-acid.

The two formulæ which, along with XXXII and XXXIV, fulfil the above conditions are XXXV and XXXVI.

$$\begin{array}{l} C_5H_{10}\text{:}C\text{——}C(CO_2H)\cdot CHMe\cdot CO_2H \\ \quad\; O\cdot CO\cdot CH_2 \end{array} \qquad \begin{array}{l} C_5H_{10}\text{:}C\text{——}C(CO_2H)\cdot CH_2\cdot CO_2H \\ \quad\; O\cdot CO\cdot CHMe \end{array}$$

(XXXV.) (XXXVI.)

Of these, the first, XXXV, possesses an anhydride-forming group exactly similar to that of the lactonic acid XXXII (p. 341). A substance of the formula XXXV ought, therefore, for reasons given when XXXII was considered, to behave like *αα′*-dimethylsuccinic acid and like the acid XXIX (p. 341), and form anhydrides in accordance with Scheme 1.

The formula XXXVI, on the other hand, does not contain two asymmetric carbon atoms in its anhydride-forming group, and is therefore out of the question.

It will be seen that, of the four possible formulæ, XXXIV (p. 342) is the only one which accords with the facts of the case, namely, that the dehydration of the substance proceeds according to Scheme 2.

It may be added that the *cis*-lactonic acid is converted by boiling hydrochloric acid into the *trans*-isomeride, thus completing the cycle of transformations, which in Scheme 2 is only fragmentary.

The *trans*-lactonic acid XXXIV (p. 342) was not the only product obtained by the alkaline hydrolysis of the methylated ester XXX (p. 342). There was always formed side by side with it a somewhat smaller quantity of a dibasic acid of the composition $C_{13}H_{18}O_6$. Both the dibasic acid and the lactonic acid appeared to be end-products of the reaction; that is to say, they were quite stable towards the reagent used in their preparation. The dibasic acid had properties practically identical with those of the dibasic acid $C_{12}H_{16}O_6$ (XXIV, p. 336), which was obtained by the alkaline hydrolysis of the unmethylated ester XV (p. 333). It has therefore, without much doubt, been formed in a manner precisely analogous to that in which the acid XXIV was produced, and has the structure shown in the formula XXXVII.

$$\begin{array}{c} CO_2H \\ C_5H_{10}\text{:}CH\cdot C{<}\begin{array}{c}CHMe\\C(OH)\end{array}{>}CO \\ CO_2H \end{array}$$

(XXXVII.)

Like the parent substance XXIV, the homologous acid XXXVII was isolated in *cis*- and *trans*-forms, that originally obtained being the *trans*-form.

The formation side by side of the acids XXXIV (p. 342) and XXXVII (p. 344) is readily explained if we accept the view put forward on p. 342, that the *cyclo*propane bond (4:5) of the methylated ester XXX is the first point in the molecule attacked by the alkaline reagent. For, if this is so, the substance XXXIII which is first formed may undergo disruption beside the methylated residue in two ways, corresponding with the two hydrolytic decompositions of ethyl acetoacetate. It may either split the *cyclo*butane ring between the carbon atoms (2) and (3) to give the lactonic acid XXXIV, as shown on p. 342, or it may split between the methyl-bearing carbon atom and the attached carboxyl group, giving the acid XXXVII.

$$C_5H_{10}:C<\begin{array}{l}C(CO_2Et)\cdot CMe\cdot CO_2Et\\ C(CO_2Et)\cdot CO\end{array} \longrightarrow C_5H_{10}:CH\diagup\begin{array}{l}C(CO_2H)\text{——}CMe\cdot CO_2H\\ C(CO_2H)(OH)\cdot CO\end{array}$$

(XXX.) (XXXIII.)

$$\longrightarrow C_5H_{10}:CH\diagup\begin{array}{l}C(CO_2H)\text{——}CHMe\\ C(CO_2H)(OH)\cdot CO\end{array}$$

(XXXVII.)

It is interesting once again to refer to the parent substance of which the acid XXXVII is the methyl derivative. It was noticed on p. 336 that formulæ XXIV and XXV were equally in harmony with the properties of the substance, but that for reasons there given formula XXIV was to be preferred. We have just seen that the formula which follows from this for the methylated substance enables us to explain the simultaneous production of this compound and of the lactonic acid XXXIV in a very straightforward manner. The alternative formula XXXVIII for the methylated

$$\begin{array}{c}CO_2H\\ C_5H_{10}:CH\cdot C<\begin{array}{c}C(OH)\\ \text{—}CO\text{—}\end{array}>CHMe\\ CO_2H\end{array}$$

(XXXVIII.)

dibasic acid, strictly analogous to the formula XXV, has not this advantage. Such a substance could not be produced side by side with the lactonic acid XXXIV (p. 342), except as a result of the simultaneous occurrence of two totally different sets of reactions; also the lactonic acid which one might expect to be produced along with a compound of the formula XXXVIII would have properties different from those which the lactonic acid isolated was found to possess. We therefore think that we were right in selecting formula XXIV rather than XXV.

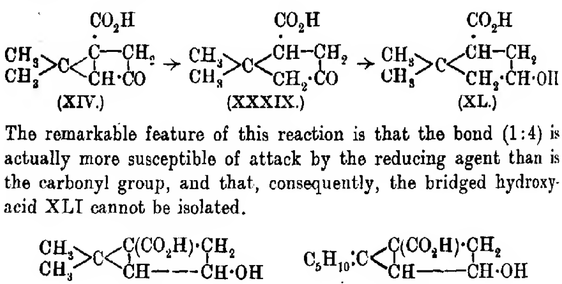
The results of the experiments on the alkaline hydrolysis of the

methylation product of the yellow sodium *spiro*-compound are summarised in table II.

These experiments have an interest, inasmuch as they confirm, and even emphasise, the remarkable instability of the bond (4:5) in the bridged-*spiro*-series. For, in spite of the fact that the entrance of the methyl group at the carbon atom (2) of the methylated ester XXX creates a point of instability between the carbon atoms (2) and (3), the reagent commences its attack, not at the bond (2:3), but at the bond (4:5).

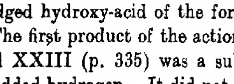
(E) *Reduction of the Monocarboxylated Bridged-ring Derivatives XIV and XXIII* (pp. 333 and 335). *Stability of the Bridge-bond* (1:4).

When the bridged-ring acid XIV is reduced by sodium amalgam, there is formed a *cyclo*pentane acid XXXIX which contains two more atoms of hydrogen than the original acid. The reduction product is a ketonic acid, and on further reduction yields the corresponding hydroxy-acid XL. The fact that the ketonic acid has been formed by the addition of hydrogen at the bridge-bond (1:4) is shown (*loc. cit.*) by the production on oxidising with nitric acid of $\beta\beta$-dimethylglutaric acid and *as*-dimethylsuccinic acid. The reduction is therefore to be represented thus:

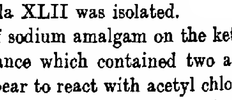


(XIV.) (XXXIX.) (XL.)

The remarkable feature of this reaction is that the bond (1:4) is actually more susceptible of attack by the reducing agent than is the carbonyl group, and that, consequently, the bridged hydroxy-acid XLI cannot be isolated.



(XLI.)

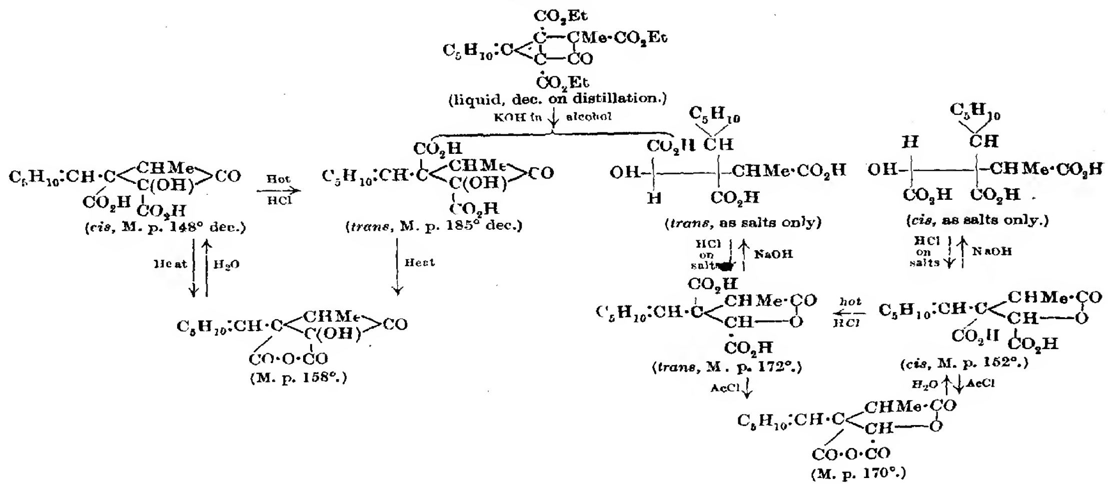


(XLII.)

A series of experiments, using the monobasic acid XXIII, yielded precisely comparable results. In spite of careful search among the products of reductions carried out under varying conditions, no bridged hydroxy-acid of the formula XLII was isolated.

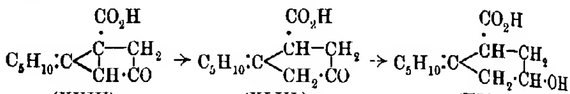
The first product of the action of sodium amalgam on the ketonic acid XXIII (p. 335) was a substance which contained two atoms of added hydrogen. It did not appear to react with acetyl chloride, but readily gave a semicarbazone. On subjecting it to further

TABLE II.



(liquid, dec. on distillation.)
KOH in alcohol
(cis, M. p. 148° dec.)
Hot HCl
(trans, M. p. 185° dec.)
(trans, as salts only)
(cis, as salts only.)
Heat
H₂O
(M. p. 158°.)
HCl on salts
NaOH
hot HCl
(trans, M. p. 172°.)
(cis, M. p. 152°.)
AcCl
(M. p. 170°.)

reduction by sodium amalgam, two more atoms of hydrogen were taken up, and there was formed a substance which gave an acetyl derivative on treatment with acetyl chloride. The successive reductions are therefore apparently analogous in the dimethyldi*cyclo*pentane and *cyclo*hexane*spiro*di*cyclo*pentane series, and in the latter case may be represented thus:



(XXIII). (XLIII.) (XLIV.)

The fact that it was really the bond (1:4), and not the bond (4:5) or the bond (5:1), which had been broken by the reducing agent was clearly proved by the manner in which the reduced substances behaved with oxidising agents. These experiments are dealt with in Section F.

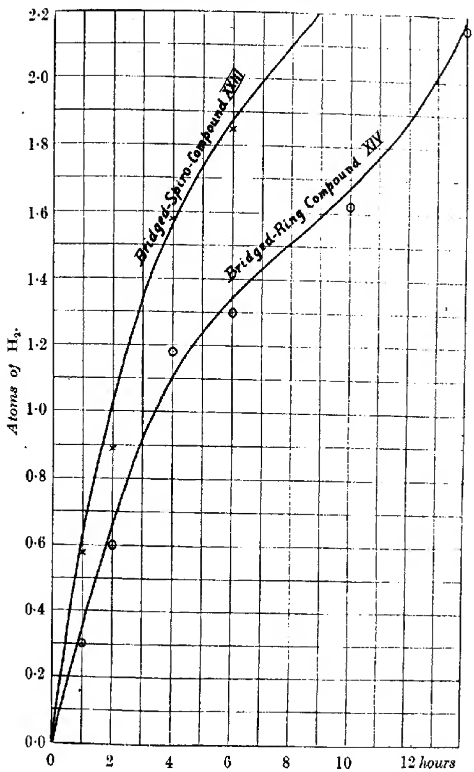
In our earliest experiments on the reduction of the bridged ketonic acid XXIII, we used conditions which were known to give a good yield of the reduced acid XXXIX when applied to the reduction of the bridged ketonic acid XIV. As a result, we obtained a product of indefinite melting point, which proved to be a mixture of the ketonic and hydroxy-acids XLIII and XLIV. It was therefore apparent that the reduction was proceeding more easily in the bridged-*spiro*-series than in the bridged-ring series.

In order to establish this point more definitely, a series of comparative experiments were instituted. In the first place, the bridged ketonic acid XIV (p. 333) was reduced under standard conditions for different lengths of time, and the products were isolated. They were, in general, a mixture of three acids, XIV, XXXIX, and XL. The proportion of hydroxyl group in this mixture was determined by estimating the acetic acid obtained by acetylation and subsequent hydrolysis. This method was found to give good results when applied to the pure hydroxy-acid XLIV. In this way, a certain time of reduction was discovered during which no appreciable quantity of hydroxy-acid was produced. The hydrogen content was determined by combustion, and it was found that the formation of hydroxy-acid began to be appreciable after the addition of about 1·7 atoms of hydrogen to the molecule. A similar set of experiments with the bridged ketonic acid of the *spiro*-series showed that the production of hydroxy-acid in this case became appreciable only after the addition of about 1·9 atoms of hydrogen to the molecule. The two bridged ketonic acids XIV and XXIII were then reduced under the same standard conditions for a certain length of time, the same in both cases, sufficiently short to ensure

that in neither case would any measurable amount of hydroxy-acid be formed. The products were then isolated and the hydrogen contents determined by combustion. Several pairs of experiments were made with different lengths of time, and the results obtained

FIG. (viii).

Fission of the bridge-bond 1 : 4.



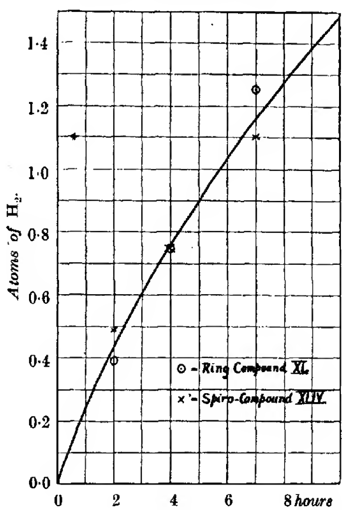
are given in the experimental part of this paper (p. 375). The figures lie fairly well on smooth but widely separated curves (Fig. viii), and, graphically interpolated, they show that if we take the time required for a 50 per cent. conversion, that is, the time during which the molecule of the bridged acid takes up one

atom of hydrogen, as the standard of comparison, then this time, in the case of the *spiro*-acid XXIII, is about 0·55 times as long as in the case of the ring derivative XIV. That is to say, the periods of half-change are in the ratio of approximately 1·8 : 1.

As a check on this result, the reduced acids XXXIX and XLIII (pp. 346 and 348) were prepared in a state of purity and further reduced under standard conditions for different lengths of time. The figures obtained in these experiments (p. 375) lie, with slight irregularities, on one and the same curve (Fig. ix). The periods

FIG. (ix).

Reduction of the ketone group.



of half-change are therefore as 1 : 1 as nearly as the experimental figures can be interpreted.

Thus there appears to be a very real difference in the ease of reduction of the monocarboxylic acids of the bridged-ring- and bridged-*spiro*-series. It will be noticed that the difference is in the sense anticipated from theoretical considerations (see Section A). It also would appear to be of the correct order of magnitude. For whilst the first-order effect, that on the bond (5 : 1), is manifested by a reaction which proceeds at a considerable speed in one series, but does not go at all in the other so far as

can be detected, both the second-order effects, that is, those on the bonds (1:2) and (1:4), exhibit themselves experimentally as moderate differences in reaction-velocities which are finite quantities in both the series. The third-order effect, that on the bond (2:3), was not detected experimentally.

(F) *Oxidation of the Fission-Products Derived from the Bridged-*spiro-*compound XII* (p. 330).

All the products of fission of the *cyclo*hexane*spiro*di*cyclo*pentane ring structure so far considered belong to one or other of the three following classes:

(1) Substances in which the bridge-bond (1:4) only has been broken.

(2) Those in which the *cyclo*propane-bond (4:5) only has been broken.

(3) Those in which the *cyclo*propane-bond (4:5) and the *cyclo*-butane-bond (2:3) have both been broken.

In order, if possible, to obtain some confirmatory evidence regarding the constitutions of these substances, at least one typical example from each class was subjected to the action of oxidising agents.

In class (1) the first substance taken was the *cyclo*hexane*spiro*-*cyclo*pentanone acid XLIII (p. 348). By far the most suitable reagent in this case is nitric acid. Dilute nitric acid, however, appears to have little action on the substance. With hot concentrated nitric acid a dibasic acid of the composition $C_8H_{12}O_4$ was obtained. This substance when distilled gave off carbon dioxide with the formation of *cyclo*hexanecarboxylic acid (hexahydrobenzoic acid). The dibasic acid is therefore evidently *cyclo*hexane-1:1-dicarboxylic acid XLV. The same dicarboxylic acid was obtained

$$\underset{\text{(XLIII.)}}{C_5H_{10}{:}C{<}\begin{matrix}CH(CO_2H)\cdot CH_2\\ CH_2\text{———}CO\end{matrix}} \xrightarrow{HNO_3} \underset{\text{(XLV.)}}{C_5H_{10}{:}C{<}\begin{matrix}CO_2H\\ CO_2H\end{matrix}}$$

when the hydroxy-acid XLIV (p. 348) was used in place of the ketonic acid.

These experiments are interesting as leaving little room for doubt that the bond broken in the reduction of the bridged-ketonic acid XXIII (p. 335) was actually the bond (1:4).

The example taken from class (2) was the *trans-cyclo*hexyl*cyclo*-butane acid XXIV (p. 336). In this case nitric acid appeared to be without effect. Warm alkaline permanganate was, however, quickly decolorised. The acid product was a liquid substance which

distilled apparently without a serious amount of decomposition and was identified as *cyclo*hexanecarboxylic acid XLVI:

$$\begin{array}{c}CO_2H\\ | \\ C_5H_{10}{:}CH{\cdot}C{<}\begin{array}{c}CH_2\\ C(OH)\end{array}{>}CO\\ | \\ CO_2H\\ \text{(XXIV.)}\end{array} \xrightarrow{KMnO_4} \begin{array}{c}C_5H_{10}{:}CH{\cdot}CO_2H\\ \\ \text{(XLVI.)}\end{array}$$

The member of the series (3) experimented on was the *trans*-β-*cyclo*hexyl-*n*-butane lactonic acid XXXIV (p. 342). This acid was also unacted on by nitric acid, and required an alkaline solution of permanganate kept at above 70° to oxidise it at all rapidly. The product was, as in the former case, *cyclo*hexylcarboxylic acid:

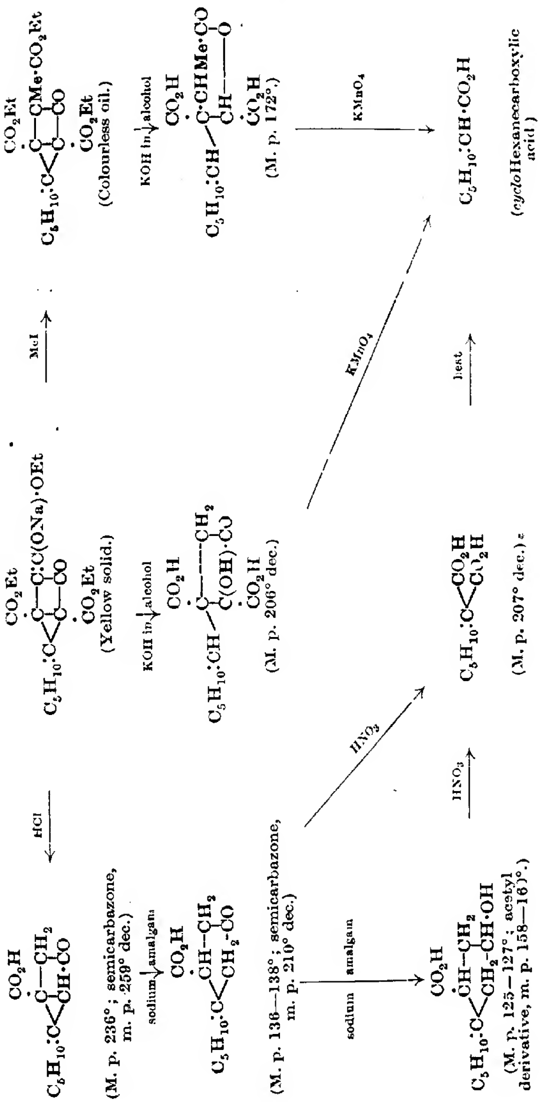
$$\begin{array}{c}Me{\cdot}CH{\cdot}CO_2H\\ | \\ C_5H_{10}{:}CH{\cdot}C{\cdot}CO_2H\\ | \\ CH(OH){\cdot}CO_2H\\ \text{(Hydroxy-acid of XXXIV.)}\end{array} \xrightarrow{KMnO_4} \begin{array}{c}C_5H_{10}{:}CH{\cdot}CO_2H\\ \\ \text{(XLVI.)}\end{array}$$

Both these oxidations with permanganate were carried out under various conditions, and in both cases the products were carefully examined for any traces of polybasic or lactonic acids, in which two side-chains might be attached to the *cyclo*hexane carbon atom. No such products were detected, and, in view of the formulæ of the oxidised substances, none would be expected. On the other hand, if, for example, in the production of the *cyclo*hexyl*cyclo*butane acid XXIV (p. 336) some bond in the di*cyclo*pentane structure other than one of those attached to the spirane carbon atom had been ruptured, one would expect to find products with two side-chains among the oxidation products.

The *cyclo*hexanecarboxylic acid XLVI obtained in the course of the above experiments appeared on careful examination to be in all cases identical with the product obtained by the reduction of benzoic acid.

The various reactions by which the di*cyclo*pentane ring in the original bridged-*spiro*-compound XII (p. 330) has been broken down forming ultimately *cyclo*hexanecarboxylic acid are summarised for convenience in table III.

TABLE III.



(G) *Examination of the By-products obtained in the Preparation of the Bridged-*spiro-*compound XII* (p. 330): *Isolation of Products of Fission Derived from this Substance through Side Reactions.*

During the preparation of the yellow sodium compound XII (p. 330) there was formed a considerable quantity of an oily by-product from which a number of acids were obtained by hydrolysis with hydrochloric acid. Amongst those isolated were *n*-butyric acid, *cyclo*hexane-1:1-diacetic acid, and *trans-cyclo*hexane*spiro*-*cyclo*propane-1:2-dicarboxylic acid. The formation of these acids is evidently traceable to the presence in the crude ethyl dibromo-*cyclo*hexanediacetate used for the condensation of the corresponding monobromo-ester, of the unbrominated ester, and of ethyl bromide as impurities. There was also obtained a *cyclo*hexane*spirocyclo*propane acid of the formula XLVII. This substance proved to be identical with the acid obtained by the action of acid hydrolysing

$$C_5H_{10}{:}C{<}\begin{array}{l}C(CO_2H){\cdot}CH_2{\cdot}CO_2H\\ |\\ CH{\cdot}CO_2H\end{array}$$

(XLVII.)

agents on the tetra-ethyl *spirocyclo*propane ester XI (p. 330), which clearly establishes the constitution of the compound.

In addition to the above-mentioned acids there were isolated two others to which the formulæ XLVIII and XLIX have been

$$C_5H_{10}{:}C{<}\begin{array}{l}\overset{CO_2H}{\dot{C}}\text{—}CHEt\\ |\qquad\ \ |\\ CH{\cdot}CO\end{array}$$

(XLVIII.)

$$\begin{array}{l}\qquad\qquad\quad Et{\cdot}CH\text{————}CO\\ C_5H_{10}{:}CH{\cdot}\overset{|}{C}{\cdot}CO_2H\quad\ \ |\\ \qquad\qquad\quad\ \overset{|}{C}H(CO_2H){\cdot}O\end{array}$$

(XLIX.)

assigned. These are clearly the products respectively of acid and of alkaline hydrolysis of the ethylated ester L. This ester is doubt-

$$C_5H_{10}{:}C{<}\begin{array}{l}C(CO_2Et){\cdot}CEt{\cdot}CO_2Et\\ |\qquad\qquad\quad\ |\\ C(CO_2Et){\cdot}CO\end{array}$$

(L.)

less produced by the action of ethyl bromide on the yellow sodium compound XII, and apparently behaves towards alkaline hydrolysing agents similarly to the corresponding methylation product XXX (p. 342). We did not investigate the action of acids on the methyl derivative XXX, but the corresponding substance XXVII (p. 341) of the dimethyldi*cyclo*pentane series was found (*loc. cit.*) to yield with acid hydrolysing agents a monocarboxylic acid, to which XLVIII is strictly analogous.

The most interesting of these substances is the fission product XLIX of the ester L, and it is of interest to examine what possibilities there are of alkaline hydrolysis of the ester L taking place. No hydrolysis to a lactone of hydroxy-ester would be likely to occur in the anhydrous alcoholic solution in which the oily by-product was formed. The oil was, however, separated from the sodium compound XII by means of 95 per cent. alcohol, and, since some sodium ethoxide would certainly be adhering to the crude sodium compound, the alcoholic washings would contain sodium hydroxide, which must have brought about the fission of the ethylated ester L.

The lactonic acid XLIX was found to possess properties practically identical with those of its prototype, the fission product XXXIV (p. 342), of the methylated bridged ester XXX. Like the lactonic acid XXXIV, it was isolated in *cis*- and *trans*-forms, the substance originally obtained being the *trans*-form. One notable point of difference was noticed between these compounds and the methylated lactonic acids previously obtained. The ethylated *cis*-lactonic acid differed from the *trans*-form, and from both forms of the lactonic acid XXXIV, in the fact that it was found possible to isolate from it the free tribasic hydroxy-acid. This substance was, however, very unstable. It slowly gave up water when exposed to air at the ordinary temperature, the product being the *cis*-lactonic acid. On boiling with hydrochloric acid it was converted into the *trans*-lactonic acid. The other relationships between these ethylated products may be seen by reference to table IV, in which they are shown in relation to the ethylated ester L, the decompositions of which form another example of the great ease with which the bond (4:5) is ruptured by alkalis.

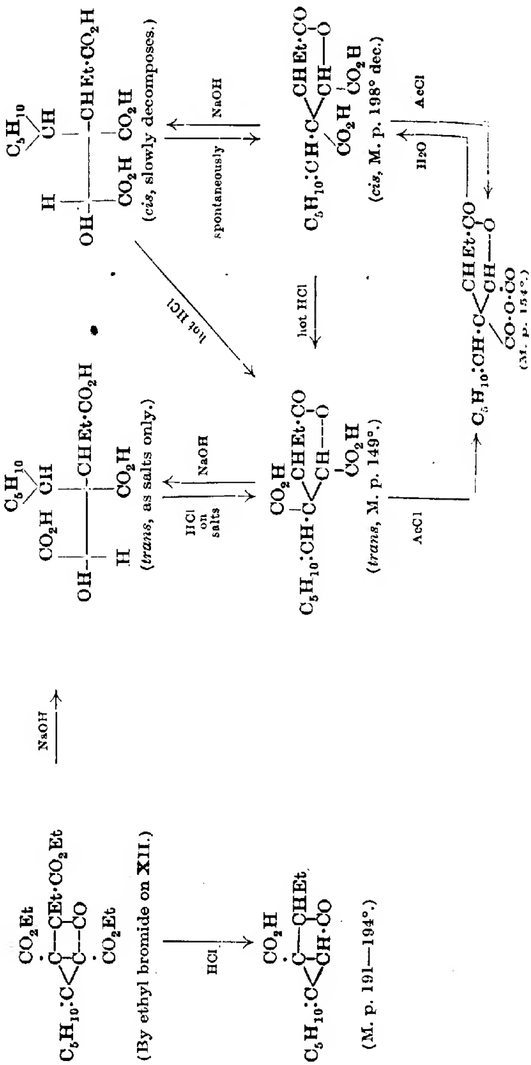
EXPERIMENTAL.

(a) *Condensation of Ethyl Dibromo*cyclo*hexane*-1:1-*diacetate with Ethyl Sodiomalonate.*

*cyclo*Hexane-1:1-diacetic acid was prepared for use in these experiments by the method given by Thole and Thorpe (T., 1911, **99**, 422).

*Ethyl Dibromo*cyclo*hexane*-1:1-*diacetate*.—The bromination of the acid was effected by the Hell-Volhard-Zelinsky method as described in Part I. of this series. The neutral product contained about 80 per cent. of dibromo-ester.

TABLE IV.



Ethyl cyclo*Hexane*spiro-1-*methyl*cyclo*propane*-1 : 1′ : 1′ : 2-*tetracarboxylate* (XI, p. 330).

Forty-six grams of the crude dibromo-ester were added to a solution, in 60 grams of alcohol, of 4·6 grams of sodium and 32 grams of ethyl malonate. The solution was boiled for three hours, and then poured into dilute hydrochloric acid. The oil was extracted with ether and the extract washed with a solution of sodium carbonate, dried, and distilled.

The ester was obtained as a colourless liquid which on redistillation boiled at 250—260°/10 mm. On boiling with hydrochloric acid it was hydrolysed with the formation of the tricarboxylic acid (XLVII, p. 354), dealt with on p. 379:

0·1209 gave 0·2708 CO_2 and 0·0849 H_2O. C=61·09; H=7·80.
$C_{21}H_{32}O_8$ requires C=61·2; H=7·8 per cent.

(b) *Formation of the Bridged*-spiro-*ester and its Sodium Compound.*

The formation of the bridged-*spiro*-compound by the condensation of the above-mentioned tetraethyl ester with itself has already been referred to in the Introduction (Section B). The compound was, however, usually prepared direct from the dibromo-ester by treating it with ethyl malonate and excess of sodium ethoxide. Many experiments were made in order to determine the best conditions.

*Ethyl Sodio*cyclo*hexane*spiro*di*cyclo*pentan*-3-*one*-1 : 2 : 4-*tricarboxylate* (XII, p. 330).

Nine grams of sodium dissolved in 140 grams of absolute alcohol were treated with 30 grams of ethyl malonate. The solution was carefully under-cooled to about 35°, and 40 grams of dibromo-ester were gradually added, the temperature being kept below 40°. Half an hour after the addition was complete the liquid was heated on a steam-bath and kept boiling for thirty hours. At the end of that time the greater part of the alcohol was boiled off, and water added to the residue in the flask. The mixture was then shaken vigorously and filtered by the aid of the pump. In these circumstances the whole of the oil precipitated by the water adhered to the solid sodium compound. The filtrate, which gave no precipitate on acidification, was discarded. The purification of the sodium compound was effected by washing on the filter with 95 per cent. alcohol, and

finally by triturating with the same solvent until the weight of the dry solid was not altered on repeating the treatment. The alcoholic filtrates contained the oily by-product. (Section j, p. 377.)

The sodium compound was obtained as a bright yellow insoluble substance which gave a crimson colour with aqueous ferric chloride containing a trace of alcohol:

0·3132 gave 0·0590 Na_2SO_4. Na = 6·10.

$C_{19}H_{25}O_7Na$ requires Na = 5·93 per cent.

Ethyl cyclo*Hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate* (XV, p. 333).

When the yellow sodium compound was shaken with cold dilute aqueous hydrochloric acid and ether it passed quickly into solution, the yellow colour being discharged. The ethereal layer, on drying and evaporating the solvent, yielded a mass of crystals melting at 46—47°.

The ester was exceedingly readily soluble in the usual organic solvents, and did not appear capable of being easily recrystallised. It gave a crimson colour with ferric chloride, and on treating with cold aqueous sodium hydroxide yielded the original sodium compound:

0·1331 gave 0·3036 CO_2 and 0·0842 H_2O. C = 62·21; H = 7·03.

$C_{19}H_{26}O_7$ requires C = 62·3; H = 7·1 per cent.

(c) *Comparative Experiments on the Formation of the Bridged-ring- and Bridged-*spiro-*compounds* (IX and XII, p. 330).

ββ-Dimethylglutaric acid was prepared by the method of Thole and Thorpe (T., 1911, **99**, 422).

Ethyl Dibromodimethylglutarate.—The acid was first converted into its anhydride (T., 1899, **75**, 48), which was then brominated (T., 1901, **79**, 776). The dibromo-ester was redistilled and collected for use in subsequent experiments at 182—185°/24 mm.

*Ethyl 1:3:3-Trimethyl*cyclo*propane-1:1′:1′:2-tetracarboxylate.*

This ester was prepared by condensing the dibromo-ester with ethyl sodiomalonate in alcoholic solution under the conditions used by Perkin and Thorpe (*ibid.*) and purified by distillation, the fraction boiling at 231—236°/34 mm. being taken as sufficiently pure for the experiments hereunder described.

Ethyl trimethyl*cyclo*propanetetracarboxylate and ethyl *cyclo*-

hexane*spiro*methyl*cyclo*propanetetracarboxylate were then employed in a series of experiments, which were carried out with the object of determining the relative speeds with which the two esters underwent internal condensation in the presence of sodium ethoxide. The method was as follows: One molecular proportion of each ester was treated with two atomic proportions of sodium dissolved in fifteen molecular proportions of absolute ethyl alcohol. The solutions were kept in a thermostat for known lengths of time, after which the alcohol was boiled off under diminished pressure, and water was added. The precipitates were then collected, washed with alcohol, dried, and weighed.

The following percentage yields of the sodium compounds IX and XII (p. 330) were obtained, the temperature being 75°:

TABLE V.

Time (hours).	Bridged-ring-compound, IX. (Per cent.)	Bridged-*spiro*-compound, XII. (Per cent.)
1·0	49·8	10·1
2·0	64·7	17·9
4·0	73·0	25·5
7·0	76·6	32·4
10·0	75·3	32·9
14·0	75·3	—
24·0	—	37·7

(d) *Hydrolysis of the Bridged*-spiro-*ester and of its Yellow Sodium Compound.*

The remarkable diversity in the characters of the substances which can be obtained by hydrolysing the yellow sodium *spiro*-compound or the corresponding free ester under different conditions has already been alluded to in the Introduction. The following is a summary of the principal experimental details.

*Diethyl Potassium Potassio*cyclo*hexane*spiro*di*cyclo*pentan*-3-*one*-1:2:4-*tricarboxylate* (XVI, p. 333).

When the original yellow sodium compound was left in contact with cold alcoholic potassium hydroxide for ten hours, it gradually dissolved, and a canary-yellow potassium salt separated.

This compound was found to be insoluble in water, but quite appreciably soluble in methyl alcohol. When recrystallised from a large bulk of this solvent, it separated in long, yellow needles, which gave a violet colour with ferric chloride:

0·1354 gave 0·0580 K_2SO_4. K = 19·16.

$C_{17}H_{20}O_7K_2$ requires K = 18·8 per cent.

Diethyl Hydrogen cyclo*Hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate* (XVII, p. 333).

When the potassium salt was treated with cold dilute hydrochloric acid, a gummy precipitate was obtained. This could not be induced to crystallise, and on distillation underwent extensive decomposition. It was therefore extracted with pure ether, and, after drying and evaporating the solvent, left for some days in an exhausted desiccator:

0·1249 gave 0·2751 CO_2 and 0·0730 H_2O. C=60·07; H=6·50.
$C_{17}H_{22}O_7$ requires C=60·4; H=6·5 per cent.

This acid-ester is also the first product of the action of boiling hydrochloric acid on the triethyl ester (XV, p. 333), as is proved by the following experiment. The yellow sodium compound was boiled with 20 per cent. hydrochloric acid for one hour. The liquid was evaporated, and the residue dissolved in the minimal quantity of water. The hot aqueous solution was rapidly cooled, and the oily precipitate which separated was collected by pouring the liquid through a wet filter. The oil on the filter was then washed through with alcohol, and caused to crystallise as completely as possible from 15 per cent. alcohol. The crystals consisted of the ethyl hydrogen ester XXI (p. 335). The ultimate oily residue from these crystallisations was dissolved in methyl alcohol and treated with a slight excess of cold methyl-alcoholic potassium hydroxide. The yellow precipitate which immediately separated was collected and recrystallised from methyl alcohol. On analysis, it gave K=19·03, whilst the free acid-ester obtained on acidification gave C=60·21, H=6·60 per cent.

With ferric chloride, the acid-ester gave a violet coloration. Cold methyl-alcoholic potassium hydroxide converted it into the potassium compound. It distilled at about 200—260°/23 mm., with, however, considerable decomposition. Attempts were made to hydrolyse the gummy distillate both by acids and by alkalis, but no pure substance was isolated from the products.

Ethyl Dihydrogen cyclo*Hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate* (XVIII, p. 334).

Five grams of the yellow sodium compound were suspended in 20 c.c. of 3*N*-ethyl-alcoholic potassium hydroxide, and the mixture was boiled until the yellow colour was discharged. The colourless precipitate, which was very hygroscopic, was collected as rapidly as possible and drained on porous porcelain in a desiccator. I

was then dissolved in a small quantity of water and decomposed with hydrochloric acid. The acid which separated out was recrystallised from water. The potassium salt XVI may be used in place of the sodium compound in this preparation.

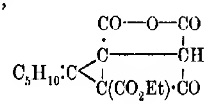
The same acid-ester may also be obtained by acid hydrolysis of the triethyl ester (XV, p. 333) or of its sodium compound. Thus, when the sodium compound was boiled for one hour with 20 per cent. hydrochloric acid, and the acid-esters XVII and XXI separated by precipitating them together as an oil in the manner described on p. 360, it was found that in the filtrate from the oil there were present two crystalline substances. These were isolated by treating the solution, after concentration, with sufficient concentrated hydrochloric acid to clear the turbidity. The crystals which were then deposited from solution were separated by fractionally crystallising from water into the acid-ester XVIII and the dibasic acid XXII, the latter being the more readily soluble.

The acid-ester formed long, colourless needles, which melted and decomposed at 206°. It gave a bluish-violet colour with ferric chloride:

0·1298 gave 0·2745 CO_2 and 0·0683 H_2O. C=57·68; H=5·84.

$C_{15}H_{18}O_7$ requires C=58·1; H=5·8 per cent.

The *anhydro-ester*,



vas prepared by treating the acid-ester at 100° for one hour with .cetyl chloride in a closed flask. The residue obtained on vaporation was crystallised from ether. The crystalline anhydride nelted at 126°, and was converted into the original acid-ester on oiling with water:

0·0751 gave 0·1705 CO_2 and 0·0385 H_2O. C=61·92; H=5·70.

$C_{15}H_{16}O_6$ requires C=61·6; H=5·5 per cent.

Ethyl Hydrogen 5-cyclo*Hexane*spiro*di*cyclo*pentan*-3-*one*-1:4-*dicarboxylate* (XXI, p. 335).

The formation of this substance has already been alluded to on . 360. It is best prepared by boiling the triethyl ester (XV, . 333) with 20 per cent. hydrochloric acid for five hours, or by oiling the acid-ester (XVIII, p. 334) with the same reagent for wo hours. In either case, the product obtained on evaporation as found to be a mixture of three acids. It was crystallised from

the minimal quantity of boiling 50 per cent. ethyl alcohol. The crystals which separated consisted principally of the monobasic acid (XXIII, p. 335), and were collected, the filtrate being then evaporated until most of the alcohol had been removed. It was then cooled as rapidly as possible, and the oil which separated was collected on a wet filter. The filtrate, on concentrating and mixing with concentrated hydrochloric acid, deposited the dibasic acid (XXII, p. 335). The oil on the filter was dissolved in alcohol and recrystallised several times from a mixture of alcohol and water.

The acid-ester obtained in this way melted at 104—106°, and gave no colour with ferric chloride. It did not decompose appreciably when heated to 250°:

0·0887 gave 0·2061 CO_2 and 0·0548 H_2O. C=63·37; H=6·88.
$C_{14}H_{18}O_5$ requires C=63·2; H=6·8 per cent.

0·1200 required 18·62 c.c. of $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{14}H_{18}O_5$ (monobasic) requires 18·6 c.c.

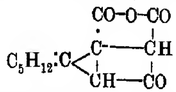
5-cyclo*Hexane*spiro*di*cyclo*pentan*-3-*one*-1 : 2-*dicarboxylic Acid* (XXII, p. 335).

The formation of this substance as a by-product in the preparation of the various acid-esters of the series has already been noticed. It was found to be produced in good yield by boiling either the yellow sodium compound or the acid-ester (XVIII, p. 334) with 10 parts by weight of 20 per cent. aqueous hydrochloric acid for twelve hours. As the boiling proceeded, oily products separated out, and subsequently passed again into solution. Then crystals appeared in the boiling liquid. At the end of the period, the mixture was cooled and allowed to remain at the ordinary temperature for twenty-four hours, after which practically the whole of the organic material had crystallised out. The crystalline mixture consisted of about three parts of the dibasic acid XXII to one part of the monobasic acid XXIII (p. 335). It was boiled with four times its weight of water, and the suspension cautiously cooled and quickly filtered. By this means, the monobasic acid was separated almost quantitatively from a solution which, in the cold, was supersaturated with respect to the dibasic acid. The agitation caused by filtering usually caused the filtrate to set to a stiff paste of crystals of the dibasic acid. These were recrystallised from water.

The acid separated from water in rosettes of long, silky, needle-shaped crystals, which melted and decomposed at 234°. It gave a deep crimson colour with ferric chloride, but did not appear to be acted on when boiled with hydrochloric acid for several days:

0·1087 gave 0·2407 CO_2 and 0·0584 H_2O. C=60·39; H=5·97.
$C_{12}H_{14}O_5$ requires C=60·5; H=5·9 per cent.

0·0715 required 24·65 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{12}H_{14}O_5$ (dibasic) requires 24·7 c.c.

The *anhydride*,  , was produced when the ree acid was treated with acetyl chloride at 100° in a closed flask. The solid residue obtained on evaporation was triturated with aqueous sodium hydrogen carbonate and recrystallised from ether. t melted at 154°, and on treating with aqueous sodium hydroxide gave the sodium salt of the original dibasic acid:

0·1050 gave 0·2515 CO_2 and 0·0518 H_2O. C=65·32; H=5·48.
$C_{12}H_{12}O_4$ requires C=65·5; H=5·5 per cent.

5-cyclo*Hexane*spiro*di*cyclo*pentan*-3-*one*-1-*carboxylic Acid* (XXIII, p. 335).

A mixture of about one part of this acid to three parts of the dibasic acid (XXII, p. 335) was formed when either the triethyl ester, XV, or its sodium compound, or the diethyl hydrogen ester, XVII, or its potassium compound, or the ethyl dihydrogen ester, XVIII, was boiled for twelve hours with 20 per cent. hydrochloric acid. The ethyl hydrogen ester XXI was found to be converted quantitatively into the monobasic acid by boiling hydrochloric acid. The dibasic acid XXII, on the other hand, did not appear to be affected by this reagent.

The dibasic acid, when heated above its melting point, however, evolved carbon dioxide, and from the dark-coloured residue a small amount of monobasic acid could be isolated. A good yield was obtained when the dibasic acid was heated with water at 200° for about ten minutes. The acid-esters XVII and XVIII also gave excellent yields of the monobasic acid when treated in this way. The triethyl ester XV, however, required the presence of a trace of acid in the water. A small quantity of hydrochloric acid or acetic acid, or even of butyric acid, was found to be sufficient.

The most convenient way of preparing the monobasic acid is by heating the yellow sodium compound with a slight excess of dilute hydrochloric acid at 200°. When preparing considerable quantities, however, it was found desirable to drive off as much carbon dioxide and alcohol as possible before closing the vessel. The

sodium compound, in portions of about 10 grams, was boiled with ten times its weight of 20 per cent. hydrochloric acid for twelve hours in a strong flask provided with a short reflux air-condenser. Enough aqueous sodium hydroxide was then added to reduce the concentration of free mineral acid to 2 or 3 per cent., and the solution was again boiled to expel the air. The flask was then securely corked and immersed in an oil-bath at 200° for ten minutes. After cooling to the ordinary temperature, the crystals were collected and recrystallised from 96 per cent. alcohol, using a little animal charcoal to remove the dark impurities. The yield was 85 per cent.

The monobasic acid was sparingly soluble in hot or cold water and in most cold organic solvents, but it crystallised well from hot ethyl alcohol in long needles. It melted at 236° without decomposition, and gave no colour with ferric chloride. It was found to be unacted on by boiling aqueous or alcoholic potassium hydroxide, and by prolonged boiling with hydrochloric acid. Cold alkaline permanganate was, however, instantly decolorised:

0·1337 gave 0·3310 CO_2 and 0·0860 H_2O. C=67·52; H=7·14.

$C_{11}H_{14}O_3$ requires C=68·0; H=7·2 per cent.

The *semicarbazone*, $C_5H_{10}\text{:}C<\begin{matrix}C(CO_2H)\cdot CH_2 \\ | \qquad\quad | \\ CH\text{———}C\text{:}N\cdot NH\cdot CO\cdot NH_2\end{matrix}$, was prepared by boiling the acid with an aqueous solution of semicarbazide acetate for a few seconds. On cooling the solution, the semicarbazone separated out, and was recrystallised from alcohol. It melted and decomposed at 259°:

0·1071 gave 0·2240 CO_2 and 0·0661 H_2O. C=57·04; H=6·85.

$C_{12}H_{17}O_3N_3$ requires C=57·4; H=6·8 per cent.

trans-3-*Hydroxy*-4-cyclo*hexyl*cyclo*butan-2-one*-3:4-*dicarboxylic Acid* (XXIV, p. 336).

Five grams of the yellow sodium compound were boiled with 30 c.c. of 4*N*-alcoholic potassium hydroxide, the boiling being continued for one hour after the suspended matter had become colourless; or, alternatively, 5 grams of the acid-ester (XVIII, p. 334) were boiled with 30 c.c. of the same reagent for one hour. In either case, the product was isolated by evaporating the alcohol and adding water and hydrochloric acid. The acid solution was extracted ten times with its own volume of ether, and the extract dried over calcium chloride for at least three days. This was found to be necessary, since the acid was present in the ether in its hydrated form, which apparently gave up water to the calcium chloride very slowly, and incomplete dehydration interfered with

the subsequent purification. When quite dry, the ether was evaporated and the viscid residue triturated with chloroform. The crystals which were caused to separate by this treatment were drained on porous porcelain and washed with fresh ether.

The acid prepared in this way was fairly pure and melted and decomposed at 203°. It was very readily soluble in water and in all the usual organic solvents, except chloroform and light petroleum. In these solvents it was only sparingly soluble, but it did not appear to crystallise well from mixtures of solvents. It gave no colour with ferric chloride, and did not appear to be acted on by boiling acetyl chloride (compare Part I). The acid was purified for analysis through the hydrate (see below):

0·1331 gave 0·2734 CO_2 and 0·0748 H_2O. C=56·02; H=6·24.
$C_{12}H_{16}O_6$ requires C=56·2; H=6·2 per cent.

0·0352 required 11·25 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{12}H_{16}O_6$ (dibasic) requires 11·3 c.c.

The *hydrated* form, $C_{12}H_{16}O_6,2H_2O$, separated in large, dense prisms when the anhydrous acid was dissolved in hot water and the solution cooled. The hydrated acid readily dissolved in dry ether, and was much more readily soluble in chloroform than the anhydrous substance. At 100°, it evolved water vapour, leaving the anhydrous acid in a very pure form, melting at 206° to a colourless liquid, which evolved steam, and, after cooling, set to a solid mass, which melted at about 135°:

0·1648 lost 0·0201 at 100°. H_2O=12·20.
$C_{12}H_{16}O_6,2H_2O$ requires H_2O=12·3 per cent.

The *silver* salt was precipitated by silver nitrate from a neutral solution of the ammonium salt:

0·1435 gave 0·0656 Ag. Ag=45·71.
0·1729 „ 0·1929 CO_2 and 0·0473 H_2O. C=30·43; H=3·03.
$C_{12}H_{14}O_6Ag_2$ requires C=30·6; H=3·0; Ag=45·9 per cent.

The *barium* salt was precipitated from a solution of the acid in water by adding an excess of barium hydroxide:

0·1007 gave 0·0595 $BaSO_4$. Ba=34·74.
$C_{12}H_{14}O_6Ba$ requires Ba=35·1 per cent.

cis-3-*Hydroxy*-4-cyclo*hexyl*cyclo*butan*-2-*one*-3:4-*dicarboxylic Acid* (XXIV, p. 336).

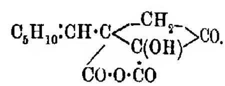
This acid was prepared by dissolving its anhydride (see below) in a slight excess of 4N-aqueous sodium hydroxide and then adding a slight excess of concentrated hydrochloric acid. The precipitated acid was collected and dried. It was then dissolved in

dry ether containing a trace of alcohol, and caused to crystallise from this solution by adding benzene. The crystals were finally purified by triturating with pure dry ether and again recrystallising from a mixture of ether and benzene containing alcohol.

The pure *cis*-acid melted at 145°, and rapidly evolved water vapour. It readily dissolved in water or alcohol, but was almost insoluble in pure dry ether. Unlike the *trans*-form, it did not appear to take up water of crystallisation:

0·0929 gave 0·1912 CO_2 and 0·0548 H_2O. C=56·13; H=6·55.
$C_{12}H_{16}O_6$ requires C=56·3; H=6·3 per cent.
0·0446 required 14·40 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{12}H_{16}O_6$ (dibasic) requires 14·3 c.c.

The Anhydride of the cis-*Acid*,

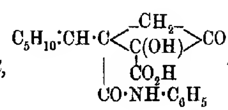


The *trans*-acid, on heating above its melting point, gave off water vapour. The transformation was, however, by no means complete unless the fused material was raised to 240—250° and maintained at this temperature until it began to darken in colour. The product solidified on cooling, and, after triturating with aqueous sodium hydrogen carbonate and drying, was recrystallised from dry ether. It separated in large, oblique prisms which melted at 155°. The substance was also recrystallised from benzene.

The same anhydride was obtained by heating the *cis*-acid above its melting point:

0·1335 gave 0·2959 CO_2 and 0·0709 H_2O. C=60·45; H=5·90.
$C_{12}H_{14}O_5$ requires C=60·5; H=5·9 per cent.

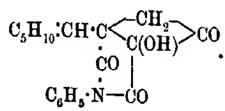
The cis-*Anilic Acid*,



This substance was at once precipitated when the *cis*-anhydride was dissolved in benzene and treated with a solution of aniline in the same solvent. It was purified by first triturating with ether and then recrystallising from dilute alcohol. It separated in minute crystals, which melted and decomposed at 202°:

0·1145 gave 0·2721 CO_2 and 0·0666 H_2O. C=64·81; H=6·46.
$C_{18}H_{21}O_5N$ requires C=65·3; H=6·3 per cent.

The cis-*Anil*,



The *cis*-anil was readily obtained by heating the anilic acid at 210° until the evolution of steam had ceased. The product was triturated with sodium hydrogen carbonate and then recrystallised from absolute alcohol. It separated in long, silky needles which melted at 199°:

0·1098 gave 0·2778 CO_2 and 0·0592 H_2O. C=69·00; H=5·99.
$C_{18}H_{19}O_4N$ requires C=69·0; H=6·1 per cent.

(e) *Comparative Experiments with the Acid-Esters* (XXVI, p. 337, *and* XVIII, p. 334) *of the Dimethyldi*cyclo*pentane and* cyclo*Hexane*spiro*di*cyclo*pentane Series*.*

One molecular proportion of each acid-ester was boiled for fifteen minutes with 6 molecular proportions of potassium hydroxide in 3·6*N*-solution in ethyl alcohol. The bulk of the alcohol was evaporated under diminished pressure and water and excess of hydrochloric acid were added to the residue. The acid products were then extracted quantitatively with ether. The percentage yields were as follows:

TABLE VI.

Bridged-ring-acid-ester XXVI.			Bridged-*spiro*-acid-ester XVIII.		
Acid-ester recovered.	Monocarboxylic acid formed.	Fission product formed.	Acid-ester recovered.	Products of loss of 4-carbethoxyl group.	Fission products formed.
85	1·5	0	0	0	85
81	4	0	5	0	78

In all cases a small quantity of gummy material was formed, and for this reason the whole of the original material was never accounted for as crystalline products. The small quantity of monocarboxylic acid XIV was readily isolated by reason of its sparing solubility in cold water. The recovered acid-ester XVIII was also quite easily separated from the fission product by means of dry chloroform in which the latter, if quite anhydrous, is almost insoluble.

* See note, p. 337.

(f) *Preparation and Hydrolysis of the Methylation Product of the Yellow Sodium* spiro-*Compound* (XII, p. 330).

The yellow sodium compound does not react at all readily with methyl iodide under the usual conditions even at 100° in a closed flask. If, however, four or five times the theoretical quantity of methyl iodide is used, methylation proceeds rapidly.

Ethyl cyclo*Hexane*spiro-2-*methyldi*cyclo*pentan*-3-*one*-1:2:4-*tricarboxylate* (XXX, p. 342).

Twenty grams of the yellow sodium compound were heated with a solution of 20 grams of methyl iodide in 100 grams of absolute alcohol at 100° for one and a-half hours in a closed flask, which, from time to time, was vigorously shaken. The excess of the methyl iodide and most of the alcohol were then distilled off and the residue poured into 400 c.c. of water. The precipitated oil was extracted with ether, the extract being washed with water and sodium carbonate solution, dried, and evaporated. The oily residue was found to decompose on attempting to distil it under diminished pressure. It was therefore allowed to remain in an exhausted desiccator for several days and then analysed:

0·1109 gave 0·2556 CO_2 and 0·0729 H_2O. C=62·86; H=7·30.

$C_{20}H_{28}O_7$ requires C=63·2; H=7·4 per cent.

The figures quoted are those for one of three closely agreeing analyses. They indicate that a partial conversion into the methyl diethyl ester has taken place:

$C_{19}H_{26}O_7$ requires C=62·2; H=7·0 per cent.

This is perhaps a natural result of the use of a large excess of methyl iodide in the preparation.

trans-*Lactonic Acid of γ-Hydroxy-β-*cyclo*hexyl-α-methyltricarballylic Acid* (XXXIV, p. 342).

Twenty-five grams of the methylated ester were boiled under a reflux condenser with 170 c.c. of 4*N*-alcoholic potassium hydroxide for two and a-half hours. The mixture was then cooled and the precipitated salts were collected and drained on porous porcelain in a desiccator. They were then dissolved in water and the solution was acidified and repeatedly extracted with ether. The residue left after drying and evaporating the extract was caused to deposit crystals by triturating with benzene, the process being repeated until an ultimate gummy residue was obtained, from which no crystals would separate.

The crystals were placed in a test-tube with just sufficient benzene to cover them. The benzene was then boiled for a few minutes and the suspension filtered while hot. The filtrate on cooling deposited crystals of the lactonic acid.

The ultimate gummy residue was esterified with alcohol and sulphuric acid in the usual way, and, after adding water, the esters were extracted with ether. From the extract the acid products were shaken out with aqueous sodium hydroxide, and again extracted from the aqueous solution after acidification. The residue obtained on evaporating the ether was hydrolysed by boiling hydrochloric acid. After twelve hours the liquid was rendered alkaline and extracted with ether, then re-acidified, and again extracted with ether. On drying and evaporating the latter extract a residue was obtained which, when treated with benzene, yielded a further quantity of the crystalline lactonic acid.

The substance, after recrystallisation from benzene, melted at 172° without decomposition, and did not appear to decompose appreciably at 260°. It dissolved very readily in water or alcohol, and fairly readily in benzene or chloroform:

0·1310 gave 0·2774 CO_2 and 0·0800 H_2O. C=57·75; H=6·78.

$C_{13}H_{18}O_6$ requires C=57·8; H=6·7 per cent.

The *silver* salt was at once precipitated when silver nitrate was added to a boiled solution of the lactonic acid in ammonia:

0·1118 gave 0·0449 Ag. Ag=44·63.

$C_{13}H_{16}O_6Ag_2$ requires Ag=44·6 per cent.

trans-γ-*Hydroxy*-β-cyclo*hexyl*-α-*methyltricarballylic Acid*.

The hydroxy-acid appeared to be stable only in the form of its salts, and in spite of several attempts it was not found possible to obtain it free. However, when the *trans*-lactonic acid was dissolved in water and slowly titrated with barium hydroxide an end-point corresponding with the neutralisation of three carboxyl groups was obtained:

0·0434 of the *trans*-lactonic acid required 19·90 c.c. $Ba(OH)_2$ solution (0·0243*N*) for complete neutralisation. $C_{13}H_{18}O_6$ changing in solution to $C_{13}H_{20}O_7$ (tribasic) requires 19·85 c.c.

The *barium* salt was prepared by treating a solution of the *trans*-lactonic acid in water with an excess of aqueous barium hydroxide:

0·1671 gave 0·1202 $BaSO_4$. Ba=42·34.

$(C_{13}H_{17}O_7)_2Ba_3$ requires Ba=42·0 per cent.

cis-*Lactonic Acid of γ-Hydroxy-β-*cyclo*hexyl-α-methyltricarballylic Acid* (XXXIV, p. 342).

This substance was readily obtained by dissolving its anhydride (see below) in boiling sodium hydroxide solution, and acidifying with hydrochloric acid. Microscopic crystals separated and were recrystallised from water.

The *cis*-lactonic acid melted at 152° with the immediate elimination of water vapour. It was more readily soluble in water than the *trans*-acid:

0·1182 gave 0·2489 CO_2 and 0·0724 H_2O. C=57·43; H=6·81.
$C_{13}H_{18}O_6$ requires C=57·8; H=6·7 per cent.

The *silver* salt was prepared by adding a solution of silver nitrate to a boiled solution of the *cis*-lactonic acid in ammonia:

0·1029 gave 0·0457 Ag. Ag=44·41.
$C_{13}H_{16}O_6Ag_2$ requires Ag=44·6 per cent.

On boiling with concentrated hydrochloric acid the *cis*-lactonic acid was partly converted into the *trans*-isomeride.

cis-*γ-Hydroxy-β-*cyclo*hexyl-α-methyltricarballylic Acid.*

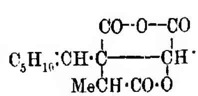
Like the *trans*-modification, this substance appeared to be stable only in the form of its salts. The *cis*-lactonic acid on titration with aqueous barium hydroxide gave, however, an end-point corresponding with salt-formation in respect of three carboxyl groups:

0·0260 of the *cis*-lactonic acid required 11·9 c.c. $Ba(OH)_2$ solution (0·0243*N*) for complete neutralisation. $C_{13}H_{18}O_6$ changing in solution to $C_{13}H_{20}O_7$ (tribasic) requires 11·9 c.c.

The *barium* salt was precipitated from a solution of the *cis*-lactonic acid in water by the addition of an excess of barium hydroxide solution:

0·1403 gave 0·1011 $BaSO_4$. Ba=42·42.
$(C_{13}H_{17}O_7)_2Ba_3$ requires Ba=42·0 per cent.

The cis-*Lactonic Anhydride,*



The lactonic anhydride was prepared by heating the *trans*-lactonic acid with acetyl chloride at 100° in a closed flask. The product was evaporated in a vacuum and the residue crystallised from ether,

when it separated in small crystals melting at 170°. It could also be purified by distillation under diminished pressure.

The same anhydride was also obtained by boiling the *cis*-lactonic acid with acetyl chloride at atmospheric pressure:

0·1170 gave 0·2637 CO_2 and 0·0679 H_2O. C=61·47; H=6·45.
$C_{13}H_{16}O_5$ requires C=61·9; H=6·3 per cent.

trans-3-*Hydroxy*-4-cyclo*hexyl*-1-*methyl*cyclo*butan*-2-*one*-3:4-*dicaroxylic Acid* (XXXVII, p. 345).

The portion of the crystalline mixture obtained in the preparation of the *trans*-lactonic acid (p. 369) which did not diissolve in the boiling benzene consisted essentially of the *cyclo*butane acid XXXVII, and was recrystallised from aqueous alcohol.

The ethereal solution of the esterified gummy residue (p. 369), after shaking out the acid products with aqueous sodium hydroxide, was dried and evaporated. The residue, on distillation under diminished pressure, yielded a fraction passing over at about 260°/25 mm., which was hydrolysed by boiling hydrochloric acid. The product was rendered alkaline and extracted with ether, then acidified, and again extracted with ether. The latter extract, on drying, and evaporating the solvent, yielded a residue which deposited crystals of the *cyclo*butane acid on adding benzene. The crystals were washed with benzene and recrystallised from aqueous alcohol.

The *trans-cyclo*butane acid melted and evolved steam at 185°, without appreciable discoloration. The liquid, on cooling, solidified, and on re-heating melted at about 140°:

0·1008 gave 0·2132 CO_2 and 0·0618 H_2O. C=57·68; H=6·81.
$C_{13}H_{18}O_6$ requires C=57·8; H=6·7 per cent.
0·0600 required 18·37 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{13}H_{18}O_6$ (dibasic) requires 18·3 c.c.

cis-3-*Hydroxy*-4-cyclo*hexyl*-1-*methyl*cyclo*butan*-2-*one*-3:4-*dicarboxylic Acid* (XXXVII, p. 345).

The *cis*-acid was prepared by boiling its anhydride (see below) with water. On cooling the solution the anhydride separated in the pure condition.

The acid melted at 148° with the immediate elimination of water-vapour. It was more readily soluble in water than the *trans*-modification:

0·0704 gave 0·1497 CO_2 and 0·0430 H_2O. C=57·99; H=6·78.
$C_{13}H_{18}O_6$ requires C=57·8; H=6·7 per cent.
0·0481 required 14·65 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{13}H_{18}O_6$ (dibasic) requires 14·7 c.c.

When boiled for four hours with concentrated hydrochloric acid the *cis*-acid was quantitatively converted into the *trans*-isomeride.

Anhydride of the cis-*Acid*, $C_5H_{10}\!:\!CH\cdot C\!<\!{CHMe \atop C(OH)}\!>\!CO.$ (with $CO\cdot O\cdot CO$ bridging the C and the C(OH))

At its melting point the *trans*-acid evolved water-vapour, but the elimination was by no means complete at this temperature. The melted substance was therefore raised to 230° and maintained at this temperature until it began to darken in colour. The product was triturated with aqueous sodium hydrogen carbonate, dried, and recrystallised from dry ether. It melted at 158°.

The same anhydride was obtained by heating the *cis*-acid above its melting point:

0·0833 gave 0·1886 CO_2 and 0·0483 H_2O. C=61·75; H=6·44.
$C_{13}H_{16}O_5$ requires C=61·9; H=6·3 per cent.

(g) *Reduction of the Monobasic Bridged*-spiro-*acid* (XXIII, p. 335) *by Sodium Amalgam.*

It was found necessary, in order to be able to repeat the results, to standardise carefully the method of experiment. The reductions were always carried out with 3 per cent. amalgam, which passed through a 10-mesh sieve but not through a 16-mesh sieve. The solutions were contained in round-bottomed flasks of capacity two and a-half times the volume of the solution, and kept at a definite temperature. During a reduction a stream of carbon dioxide was led into the flask, but was not allowed to bubble through the liquid. These conditions apply to all the experiments described in this and the next section.

5-cyclo*Hexane*spirocyclo*pentan*-3-*one*-1-*carboxylic Acid* (XLIII, p. 348).

Five grams of the ketonic acid (XXIII, p. 335) were dissolved in an amount of sodium carbonate sufficient to give a neutral solution and the whole made up to 200 c.c. This solution was kept at 14° by immersing it in cold water and reduced under the standard

conditions by adding 10 grams of amalgam once every half hour until 120 grams in all had been used. Half an hour after the addition of the last of the amalgam the mercurial layer was removed and the aqueous layer acidified. The oily precipitate was allowed to solidify and was then collected and recrystallised from dilute alcohol.

The acid melted at 136—138°, and was found to be very readily soluble in all usual organic solvents except light petroleum; in this solvent, as in water, it was sparingly soluble:

0·0867 gave 0·2145 CO_2 and 0·0635 H_2O. C=67·49; H=8·14.
$C_{11}H_{16}O_3$ requires C=67·3; H=8·2 per cent.

The Semicarbazone, $C_5H_{10}:C<\begin{matrix}CH(CO_2H)\cdot CH_2 \\ CH_2\text{———}C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}$.

The semicarbazone separated when a solution in which the acid and semicarbazide acetate had been boiled together was cooled. After recrystallising from alcohol it melted and decomposed at 210°:

0·1079 gave 0·2262 CO_2 and 0·0757 H_2O. C=57·17; H=7·80.
$C_{12}H_{19}O_3N_3$ requires C=56·9; H=7·5 per cent.

5-cyclo*Hexane*spirocyclo*pentan*-3-*ol*-1-*carboxylic Acid* (XLIV, p. 348).

Five grams of the above *cyclo*pentanone acid were dissolved in a quantity of aqueous sodium carbonate sufficient to give an approximately neutral solution which was made up to 400 c.c. This solution was kept at 17° and reduced under standard conditions with 240 grams of amalgam, 10 grams being added every half hour. Half an hour after the addition of the last of the amalgam the mercurial layer was run off and the aqueous layer acidified and extracted with ether. The solid residue obtained after the ether had been dried and distilled off was recrystallised from a mixture of benzene and light petroleum.

The hydroxy-acid melted at 125—127° and was very readily soluble in all the usual organic solvents except light petroleum. It was much more readily soluble in water than was the corresponding ketonic acid:

0·1092 gave 0·2672 CO_2 and 0·0884 H_2O. C=66·93; H=9·00.
$C_{11}H_{18}O_3$ requires C=66·7; H=9·1 per cent.

Acetyl Derivative, $C_5H_{10}:C<\begin{matrix} CH(CO_2H)\cdot CH_2 \\ CH_2 \text{———} CH\cdot OAc \end{matrix}$.

When the hydroxy-acid was boiled with acetyl chloride for four hours and the solution evaporated there was left a solid residue which was recrystallised from benzene. It melted at 157—160°:

0·0887 gave 0·2122 CO_2 and 0·0680 H_2O. C = 65·24; H = 8·52.
$C_{13}H_{20}O_4$ requires C = 65·0; H = 8·3 per cent.

0·1552 gave acetic acid requiring 26·4 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{13}H_{20}O_4$ requires 26·6 c.c.

(h) *Comparative Experiments on the Reduction of the Bridged-ring- and Bridged-spiro-acids XIV* (p. 333) *and XXIII* (p. 335).

The general plan which was followed in these experiments has already been sketched in the Introduction (Section E).

The most convenient method of preparing the bridged-ring acid XIV was found to be by treating the sodium compound IX (p. 330) according to the method (p. 364) used in the preparation of the acid XXIII from the sodium compound XII. The reductions of the bridged-ketonic-acids XIV and XXIII were carried out under the usual conditions (p. 372). The experiments were conducted in pairs, using 0·80 gram of the acid XIV and 1·00 gram of the acid XXIII. The neutral solutions of the acids were immersed in the same water-bath and treated with 1 gram of amalgam every fifteen minutes so long as the experiment lasted. The aqueous layers were then acidified and extracted quantitatively with pure ether. The solid residues obtained on evaporating the solvent were allowed to remain in an exhausted desiccator for forty-eight hours.

The dried products were then analysed. Usually about 0·4 or 0·5 gram was taken and the water formed by combustion determined. In certain cases the substance was also acetylated and the product left after evaporating, desiccated over potassium hydroxide and quantitatively hydrolysed, the acetic acid being distilled off in a current of steam and estimated by titration with standard alkali. This figure gave the quantity of hydroxy-acid which had been formed in the reduction, whilst the water formed on combustion enabled one to calculate the total quantity of hydrogen which had been introduced during the reduction. The accompanying table (table VII) gives the results of these experiments, the figures within the brackets (......) representing the calculated limits.

Another set of experiments, similar to the above, was instituted

in which the reduced ketonic-acids XXXIX (p. 346) and XLIII (p. 348) were used in place of the bridged-ketonic-acids XIV and XXIII. The quantities taken for each experiment were 0·80 gram of the acid XXXIX, and 1·00 gram of the *spiro*-acid XLIII. The other quantities and conditions of experiment were the same as in the former case. In this instance the products were not acetylated and hydrolysed, but the water formed on combustion was determined. The results of these experiments are given in table VIII, the figures in brackets (......) representing, as before, the calculated limits.

TABLE VII.

		Bridged-ring-acid (0·80 gram).			Bridged-*spiro*-acid (1·00 gram).		
Time (hours).	Amalgam (grams).	Per cent. of H in product.	Atoms of H introduced.	Per cent. hydroxy-acid.	Per cent. of H in product.	Atoms of H introduced.	Per cent. hydroxy-acid.
(0	0	6·49	0·00	0	7·22	0·00	0)
1	4	6·67	0·30	—	7·49	0·58	—
2	8	6·85	0·60	—	7·64	0·89	—
4	16	7·20	1·18	—	7·97	1·58	—
6	24	7·27	1·30	0	8·09	1·85	2
10	40	7·46	1·62	3	8·30	2·30	18
14	56	7·79	2·16	21	—	—	—
(∞	∞	8·86	4·00	100	9·09	4·00	100)

TABLE VIII.

		Ring-acid (0·80 gram).		*spiro*-Acid (1·00 gram).	
Time (hours).	Amalgam (grams).	Per cent. of H in product.	Atoms of H introduced.	Per cent. of H in product.	Atoms of H introduced.
(0	0	7·69	0·00	8·16	0·00)
2	8	7·92	0·39	8·39	0·49
4	16	8·13	0·75	8·51	0·75
7	28	8·42	1·25	8·67	1·10
(∞	∞	8·86	2·00	9·09	2·00)

(i) *Oxidation of Fission-products Derived from the Bridged-*spiro-*sodio-ester XII* (p. 330).

Oxidation experiments were tried with three types of fission-product, including the *spirocyclo*pentanone acid XLIII (p. 348), the *transcyclo*hexyl*cyclo*butane acid XXIV (p. 336), and the *trans*-lactonic acid of hydroxy*cyclo*hexylmethyltricarballylic acid XXXIV (p. 342). None of these appeared to be acted on by boiling dilute nitric acid. Concentrated nitric acid, however,

readily oxidised the first of these three acids, but did not react with the last two. These, however, were readily attacked by warm alkaline permanganate. Two crystalline oxidation products, *cyclo*hexanecarboxylic acid and *cyclo*hexane-1:1-dicarboxylic acid, were obtained in the course of these experiments.

cyclo*Hexane-1:1-dicarboxylic Acid* (XLV, p. 351).

This acid was prepared by oxidising both the *spirocyclo*pentanone acid XLIII (p. 348), or the corresponding *spirocyclo*pentanol acid XLIV (p. 348), with concentrated nitric acid. The organic acid (2·5 grams) was warmed with an excess of concentrated nitric acid until most of the red fumes had been evolved. The resulting solution was then boiled for a few minutes, and finally evaporated to dryness. The residue was treated with water and again evaporated. In this way, a semi-solid mass was obtained, from which the crystals were separated by spreading on porous porcelain.

After recrystallising from water, the acid melted at 207°, with the evolution of carbon dioxide and a certain amount of discoloration:

0·1008 gave 0·2058 CO_2 and 0·0650 H_2O. C=55·68; H=7·16.
$C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.

0·0412 required 19·75 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_8H_{12}O_4$ (dibasic) requires 19·7 c.c.

cyclo*Hexanecarboxylic Acid* (*Hexahydrobenzoic Acid*).

This acid was obtained in two ways:

(1) *By distilling* cyclo*hexane*-1 : 1-*dicarboxylic acid*. The dicarboxylic acid on distillation under ordinary pressure gave off carbon dioxide and yielded a distillate, which boiled at 230—235° and solidified when cooled by ice. The crystals melted at 18—23°. (Found: C=65·42; H=9·51. Calc.: C=65·6; H=9·4 per cent.)

(2) *By oxidising* cyclo*hexyl derivatives*. Either the *trans*-lactonic acid of hydroxy*cyclo*hexylmethyltricarballylic acid XXXIV (p. 342) or the *trans*-*cyclo*hexyl*cyclo*butanone acid XXIV (p. 336) may be used. The organic acid (10 grams) was dissolved in an excess of a solution of sodium carbonate and treated with 30 grams of potassium permanganate. The permanganate was added in successive small quantities, sufficient time being allowed between each addition for the solution to become decolorised, the reaction being aided by heating. When all the permanganate had

been added and decolorised, the liquid was filtered and extracted with ether to remove any neutral oxidation products. The aqueous solution was then acidified with hydrochloric acid, and the acid products were extracted with ether. From the residue obtained on drying and evaporating the solvent, some gummy material was separated by distilling under diminished pressure, and the liquid distillate was fractionally distilled under atmospheric pressure. In this way, there was obtained a fraction boiling at 232—236°, which solidified on cooling in ice to a mass of crystals melting at 21—25°. (Found: C=65·63; H=9·51. Calc.: C=65·6; H=9·4 per cent.)

The acid prepared by both these methods melted at a temperature a few degrees lower than the recorded melting point, namely, 29° (Lumsden, T., 1905, **87**, 91). The same experience in regard to it is recorded by Haworth and Perkin (T., 1894, **65**, 103). It certainly appears to be exceedingly difficult to obtain preparations showing the correct melting point when working with small quantities of material. Crystals of the acid when left exposed to air rapidly liquefied, and it did not appear to be possible to induce the acid to separate in a crystalline form by cooling a solution in light petroleum below 0°. These observations agree precisely with the statements made by Lumsden, and, along with the analytical figures, are regarded as leaving no doubt as to the identity of the substance.

(j) *Examination of the Oily By-product obtained in the Preparation of the Bridged*-spiro-*sodio-ester XII* (p. 330).

The alcoholic solution of the oily by-product obtained during the preparation of the yellow sodium spiro-compound (p. 357) was distilled to remove the alcohol, the residue dissolved in ether and shaken with water. The ethereal solution was then dried and evaporated, the residue being distilled under diminished pressure. Three fractions were obtained: (1) below 120°/20 mm., (2) between this and 250°/11 mm., and (3) at 250—160°/11 mm., together with a small, dark-coloured, non-volatile residue.

Fraction (1).—The first fraction contained practically the whole of the ethyl malonate present in the original oil. It was redistilled, and the small residue of high boiling point was added to the second fraction, (2).

Fraction (2).—The second fraction, which did not appear to be capable of separation into pure compounds by distillation, was boiled with hydrochloric acid for forty-eight hours. During the reaction, a strong odour of butyric acid was developed. When

the hydrolysis was complete, the butyric acid was distilled off in a current of steam, and the residual solution boiled with charcoal, filtered, and evaporated to dryness. Five acids were isolated from the crystalline residue.

cyclo*Hexane*-1:1-*diacetic Acid.*—The crystalline residue was recrystallised from the minimal quantity of 35 per cent. alcohol. The crystals which separated contained three of the five acids, the separation from the other two, which remained in the mother liquor, being very nearly quantitative. The crystals melted at 160—200° approximately. They were dissolved in dilute ammonia and, after the excess of ammonia had been evaporated, were treated in the cold with a solution of zinc sulphate. The precipitate was collected, washed with cold water, and then digested with hydrochloric acid. The acid thus precipitated melted at 174—179°, and was again precipitated as its zinc salt. The free acid was then liberated and recrystallised from water, when it melted at 181°, and was identified as *cyclo*hexane-1:1-dicarboxylic acid by direct comparison with a specimen of that substance. The preparation, together with some small residues obtained subsequently, constituted 15 per cent. of the original crystalline mixture.

trans-cyclo*Hexane*spirocyclo*propane*-1:2-*dicarboxylic Acid.*

The combined filtrates from the zinc salt of *cyclo*hexane-1:1-diacetic acid were concentrated and treated with concentrated hydrochloric acid. The precipitated acids were dissolved in ammonia, and, after concentrating the solution, treated in the cold with a considerable excess of a saturated solution of lead nitrate. The lead salts were collected and recrystallised from the minimal quantity of boiling water, and then decomposed with a slight excess of dilute nitric acid. This treatment separated the last trace of *cyclo*hexanediacetic acid, which, along with a small quantity of the *trans-spirocyclo*propane acid, remained in the filtrates from the lead salt. These traces were separated by means of their zinc salts, as described above. The combined *cyclo*hexanediacetic acid-free preparations were extracted twice with three parts by weight of boiling benzene. The undissolved portion melted at 234—237°, and on recrystallisation from dilute alcohol melted sharply at 237°. It was identified as *cyclo*hexane*spiro*-*cyclo*propanedicarboxylic acid by direct comparison with a specimen. The preparation, together with some residues subsequently obtained, amounted to 65 per cent. of the original crystalline mixture.

3-*cyclo*Hexane*spiro*-1-*methyl*cyclo*propane*-1 : 1′ : 2-*tricarboxylic Acid* (XLVII, p. 354).

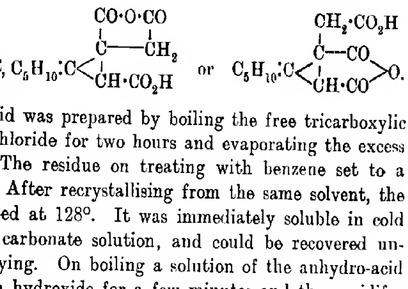
The solution in the 35 per cent. alcohol from which the above two dicarboxylic acids were crystallised (p. 378) was evaporated, and the residue resolved by crystallisation from 50 per cent. alcohol into three distinct fractions: (1) a small quantity of a mixture of the same two dicarboxylic acids, (2) a much more readily soluble, crystalline substance melting at about 208°, and (3) a viscous gum.

The first fraction was treated according to the methods already described for the separation of the two dicarboxylic acids.

The second consisted essentially of the *spirocyclo*propanetricarboxylic acid. It represented about 8 per cent. of the original crystalline mixture, and, on recrystallising from water, melted at 215°, with the immediate elimination of water vapour:

0·1156 gave 0·2386 CO_2 and 0·0675 H_2O. C=56·30; H=6·49.
$C_{12}H_{16}O_6$ requires C=56·2; H=6·2 per cent.
0·0453 required 21·95 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{12}H_{16}O_6$ (tribasic) requires 21·9 c.c.

The Anhydro-acid,



The anhydro-acid was prepared by boiling the free tricarboxylic acid with acetyl chloride for two hours and evaporating the excess of the reagent. The residue on treating with benzene set to a mass of crystals. After recrystallising from the same solvent, the anhydro-acid melted at 128°. It was immediately soluble in cold sodium hydrogen carbonate solution, and could be recovered unchanged by acidifying. On boiling a solution of the anhydro-acid in aqueous sodium hydroxide for a few minutes and then acidifying, the free tribasic acid was regenerated:

0·1548 gave 0·3418 CO_2 and 0·0823 H_2O. C=60·23; H=5·90.
$C_{12}H_{14}O_5$ requires C=60·5; H=5·9 per cent.

5-*cyclo*Hexane*spiro*-2-*ethyldi*cyclo*pentan*-3-*one*-1-*carboxylic Acid* (XLVIII, p. 354).

The two benzene filtrates obtained in the preparation of the *spirocyclo*propanedicarboxylic acid (p. 378) were combined and evaporated. The residue, which still contained about three parts

of the dicarboxylic acid to one of the bridged-monocarboxylic acid (this was indicated by a titration), was weighed, and extracted with three times its weight of boiling benzene. The extract was evaporated and the residue treated again in this way, the treatment being repeated until the residue obtained after evaporating an extract was completely soluble in three parts of boiling benzene. The product was fractionally crystallised from benzene. After a considerable number of fractional crystallisations, a preparation was obtained which did not appear to change in melting point when again recrystallised.

This substance separated from benzene in long needles, which melted at 191—194°. It was sparingly soluble in water and gave no colour with ferric chloride:

0·0610 gave 0·1537 CO_2 and 0·0432 H_2O. C=69·75; H=7·99.
$C_{13}H_{18}O_3$ requires C=70·3; H=8·1 per cent.

0·0376 required 7·20 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{13}H_{18}O_3$ (monobasic) requires 7·0 c.c.

The analytical figures, especially those for the titration, do not correspond with the formula so well as could be desired. The discrepancies are, however, all in a direction that may be taken to indicate that the preparation still contained a small quantity of the *spirocyclo*propanedicarboxylic acid, which, owing to the smallness of the quantity of material, it was not possible to remove. The preparation constituted about 0·1 per cent. of the original crystalline mixture.

trans-*Lactonic Acid of* γ-*Hydroxy*-β-cyclo*hexyl*-α-*ethyltricarballylic Acid* (XLIX, p. 354).

The viscous gum, which was obtained as the third fraction in the separation by means of 50 per cent. alcohol mentioned on p. 379, was distilled under diminished pressure. More than three-quarters of it passed over at 240—250°/40 mm., and this, on treatment with benzene, solidified to a mass of colourless crystals. These represented about 3 per cent. of the original crystalline mixture, the residue in the distilling flask, which was not further examined, accounting for about 1 per cent.

The crystalline lactonic acid, after recrystallisation from either water or benzene, melted at 149°. It dissolved readily in water and all the usual organic solvents except light petroleum:

0·1228 gave 0·2660 CO_2 and 0·0962 H_2O. C=59·08; H=7·09.
$C_{14}H_{20}O_6$ requires C=59·2; H=7·0 per cent.

The *silver* salt was precipitated by adding silver nitrate solution to a boiled solution of the lactonic acid in ammonia:

0·1063 gave 0·0461 Ag. Ag=43·37.

$C_{14}H_{18}O_6Ag_2$ requires Ag=43·4 per cent.

trans-γ-*Hydroxy*-β-cyclo*hexyl*-α-*ethyltricarballylic Acid*.

This hydroxy-acid (contrast the *cis*-form) appeared to be stable only in the form of its salts. All attempts to obtain it in the free state were unsuccessful. However, when the *trans*-lactonic acid was dissolved in water and the solution titrated slowly with barium hydroxide in the cold, an end-point corresponding with the neutralisation of three carboxyl groups was obtained:

0·0516 required 22·40 c.c. $Ba(OH)_2$ solution (0·0243*N*) for complete neutralisation. $C_{14}H_{20}O_6$, changing in solution to $C_{14}H_{22}O_7$ (tribasic), requires 22·4 c.c.

The *barium* salt was precipitated from an aqueous solution of the *trans*-lactonic acid by adding an excess of a solution of barium hydroxide:

0·1678 gave 0·1179 $BaSO_4$. Ba=41·36.

$(C_{14}H_{19}O_7)_2Ba_3$ requires Ba=40·8 per cent.

cis-*Lactonic Acid of* γ-*Hydroxy*-β-cyclo*hexyl*-α-*ethyltricarballylic Acid* (XLIX, p. 354).

The *cis*-lactonic acid was readily prepared by heating the free *cis*-hydroxy-acid (see below) at 100° for a few minutes.

When dissolved in water the lactonic acid regenerated the hydroxy-acid, which could either be crystallised out or titrated in solution. The lactonic acid could, however, be recrystallised from a mixture of benzene and light petroleum without any change taking place. It melted at 198° with the evolution of water-vapour:

0·1040 gave 0·2244 CO_2 and 0·0664 H_2O. C=58·84; H=7·10.

$C_{14}H_{20}O_6$ requires C=59·2; H=7·0 per cent.

The *silver* salt was prepared by dissolving either the *cis*-lactonic acid or the *cis*-hydroxy-acid (see below) in dilute ammonia, boiling, and adding an excess of silver nitrate solution:

0·1041 gave 0·0449 Ag. Ag=43·13.

$C_{14}H_{18}O_6Ag_2$ requires Ag=43·4 per cent.

On boiling the *cis*-lactonic acid with hydrochloric acid a partial conversion into the *trans*-lactonic acid took place.

cis-γ-*Hydroxy-β*-cyclo*hexyl-α-ethyltricarballylic Acid.*

This substance was prepared by boiling the *cis*-lactonic anhydride (see below) with a slight excess of aqueous sodium hydroxide and acidifying with hydrochloric acid. The *cis*-hydroxy-acid slowly separated out.

The substance is very unstable, and loses a molecule of water with great readiness, giving the *cis*-lactonic acid. The change was found to proceed with rapidity at 60° in an exhausted desiccator at the ordinary temperature, and slowly when the acid was exposed to air under ordinary conditions. In cold aqueous solution the substance behaved in every way as a tribasic acid:

0·1003 gave 0·2045 CO_2 and 0·0666 H_2O. C = 55·60; H = 7·38.
$C_{14}H_{22}O_7$ requires C = 55·6; H = 7·3 per cent.

0·0382 required 16·65 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{14}H_{22}O_7$ requires (tribasic) 16·6 c.c.

The *barium* salt was precipitated when the hydroxy-acid was dissolved in water and treated with an excess of barium hydroxide solution:

0·1057 gave 0·0740 $BaSO_4$. Ba = 41·18.
$(C_{14}H_{19}O_7)_2Ba_3$ requires Ba = 40·8 per cent.

When the *cis*-hydroxy-acid was boiled with 20 per cent. hydrochloric acid for some hours a partial conversion into the *trans*-lactonic acid took place.

The cis-*Lactonic Anhydride*,

$$C_5H_{10}{:}CH\cdot\begin{array}{c}CO{-}O{-}CO\\ |\qquad\;\;\; |\\ C{-\!-\!-\!-}CH\\ |\qquad\;\;\; |\\ Et\cdot CH\cdot CO\cdot O\end{array}$$

The *trans*-lactonic acid did not appear to be dehydrated to any appreciable extent when heated above its melting point or when distilled under diminished pressure. It readily eliminated water, however, when heated at 100° for half an hour with acetyl chloride. On evaporating the product and treating the residue with benzene, crystals of the lactonic anhydride were obtained. After being recrystallised from benzene the substance melted at 154°. It did not dissolve at an appreciable rate in cold aqueous sodium hydrogen carbonate, but on warming with sodium hydroxide both oxygen rings were opened up and the *cis*-hydroxy-acid was formed:

0·1023 gave 0·2356 CO_2 and 0·0625 H_2O. C = 62·81; H = 6·79.
$C_{14}H_{18}O_5$ requires C = 63·2; H = 6·7 per cent.

Fraction (3).—The third fraction which was obtained on distilling

the oily by-product (p. 377) boiled at 250—260°/11 mm. and consisted of fairly pure ethyl *cyclo*hexane*spiro*methyl*cyclo*propanetetracarboxylate (XI, p. 330). When hydrolysed with hydrochloric acid it yielded the tricarboxylic acid (XLVII, p. 354) dealt with on p. 379.

(k) *Note on Ethyl Dihydrogen* 5:5-*Dimethyldi*cyclo*pentan*-3-*one*-1:2:4-*tricarboxylate* (XXVI, p. 337).

This member of the dimethyldi*cyclo*pentane series, which was made use of in this research, has not been previously described.

The yellow sodium compound X (p. 330) was boiled with five times its weight of a 3*N*-solution of potassium hydroxide in alcohol until the suspended matter just became colourless. The precipitate was collected and drained on porous porcelain in a desiccator. It was then dissolved in the minimal quantity of water and decomposed with excess of concentrated hydrochloric acid. The crystals obtained were recrystallised from 15 per cent. hydrochloric acid.

The acid-ester melted and decomposed at 162°, and gave a purple colour with ferric chloride. It was readily converted into the monocarboxylic acid XIV (p. 333) by heating for a few minutes at 200° with a little water. When heated in the dry state, it evolved carbon dioxide and steam, and from the charred residue a small amount of the acid XIV was isolated. It is perhaps worthy of note that the monocarboxylic acid should be obtained in this way, but it is doubtless the result of the hydrolytic action of the steam which is evolved as the substance decomposes:

0·1261 gave 0·2453 CO_2 and 0·0599 H_2O. C=53·05; H=5·28.

$C_{12}H_{14}O_7$ requires C=53·3; H=5·2 per cent.

0·1070 required 32·7 c.c. $Ba(OH)_2$ solution (0·0243*N*) for neutralisation. $C_{12}H_{14}O_7$ (dibasic) requires 32·6 c.c.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON.

RESEARCH LABORATORIES, CASSEL CYANIDE COMPANY, LTD., GLASGOW.

[*Received, March* 1?*th*, 1919.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 27TH, 1919, AT 4 P.M.

SIR WILLIAM J. POPE, K.B.E., F.R.S., President, in the Chair.

Dr. T. S. PRICE and Dr. C. K. TINKLER were elected Scrutators, and the ballot was opened for the election of Officers and Council.

The Report of Council for 1917–1918 was formally presented to the meeting by the PRESIDENT. After statements by one of the Secretaries as to the progress made in the revision of the Bye-laws and by the Treasurer as to the financial position of the Society, the adoption of the Report of Council, together with the Statement of Accounts for the year ending December 31st, 1918, was proposed by Professor G. BARGER, seconded by Dr. G. W. MONIER-WILLIAMS, and carried unanimously.

REPORT OF COUNCIL, 1918–1919.

The Council are gratified to report a substantial increase in the membership of the Society. On December 31st, 1917, the number of Fellows was 3,270. During 1918, 249 Fellows were elected and 13 reinstated, making a gross total of 3,532. The Society has lost 62 Fellows by death; 16 have resigned; the elections of 6 have been declared void, and 47 have been removed for non-payment of Annual Subscriptions. The total number of Fellows, therefore, as at December 31st, 1918, was 3,401, showing an increase of 131, as compared with 72 in 1917.

It is with regret they report that the following Fellows have died on Service:

John Percy Bates (1913).
Charles William Dick (1917).
Edward Frank Harrison (1894).
Leonard Ison Pitt (1911).

and that the death of the following has also occurred:

Richard Leburn Barnes (1875).
James Bayne (1874).
William Henry Blake (1890).
Arthur Clegg Bowdler (1865).
Joseph John Bowley (1896).
Harry Broadbent (1889).
William Edward Callister (1909).
Thomas Charles Cloud (1878).
James Mason Crafts (1870).
William Adam Dixon (1862).
John Ernest Dunstan (1917).
Thomas Farries (1870).
Charles Thomas Foreman (1907).
Edward Francis (1879).
Charles James Pemeller Fuller (1896).
George Thomas Glover (1872).
Walter Augustus Handcock (1900).
Egerton Hargreaves (1909).
Henry James Helm (1872).
Richard Pendarves Hodges (1913).
Henry Tylston Hodgson (1873).
William Lamond Howie (1876).
Edward Lewis James (1912).
David Smith Jardin (1902).
Edgar Dingle Jones (1912).
John Sydney Keel (1917).
Douglas Rayment Keller (1913).
William Joel Kemp (1882).
Hassum Alidina Lakhani (1909).
Edmund Albert Letts (1879).
Thomas Stratford Logan (1902).
Thomas Watson Lovibond (1882).
Sydney Lupton (1872).
George Cannon McMurtry (1889).
Charles Stewart Maries (1918).
Edward Matthey (1884).
Elias Mendoza (1918).
Alexander Milne (1885).
Sir Alexander Pedler (1870).
Mulgrave Daniel Penney (1870).
George Frederick Tyler Phillips (1904).
William Ping (1889).
Joseph Price Remington (1886).
Alfred Gordon Salamon (1880).
John Scudamore Sellon (1875).
Alfred Senier (1875).
Walter Dalrymple Severn (1896).
John William Shepherd (1899).
Richard Spencer (1886).
James Carter Spensley (1917).
Henry Charles Stephens (1880).
Edward Cumming Thompson (1894).
John Bishop Tingle (1889).
Thomas Tyrer (1876).
Herbert William Mills Willett (1906).
Christopher Wilson (1894).
Reginald Cowdell Woodcock (1871).
John Young (1874).

Resignations have been received from:

William James Bees (1905).
Hugh Garner Bennett (1909).
Kula Bhushan Bhaduri (1903).
Frederick Raine Ennos (1914).
Nagardas Purushottam Gandhi (1915).
John Thomas Hall (1903).
Herbert Edwin Macadam (1896).
David James Morgan (1895).
Frederick Filmer de Morgan (1897).
Joseph Morris (1891).
Malur Srinivasa Rau (1910).
Abhayacharan Sanyal (1891).
Robert Greig Smith (1891).
Thomas May Smith (1910).
Alfred Tingle (1904).
James Woodward (1888).

The congratulations of the Society are offered to Professor William Odling, Past-President, elected a Fellow on January 17th, 1848, who has now completed seventy-one years as a Fellow. The Society's congratulations are also extended to:

	Elected.
Dr. Augustus George Vernon Harcourt (Past-President)......	Feb. 3rd, 1859.
John Spiller	Feb. 3rd, 1859.
Josiah Wyckliffe Kynaston........	Feb. 17th, 1859.
Thomas William Salter........	Feb. 17th, 1859.

who have been Fellows for more than sixty years, and to the following, who have attained their jubilee as Fellows:

	Elected.
John Hughes	Dec. 17th, 1868.
Edward Knowles Muspratt	Jan. 21st, 1869.
Thomas Bolas	Mar. 18th, 1869.
Frank Clowes	Mar. 18th, 1869.

The volume of Transactions for 1918 contains 995 pages, of which 849 pages are occupied by 89 memoirs, the remaining 146 pages being devoted to the Obituary Notices, three lectures on special subjects, the Report of the Annual General Meeting, and the Presidential Address. The volume for the preceding year contained 95 memoirs occupying 960 pages. The Journal for 1918 contains also 2,436 abstracts occupying 1,032 pages, whilst the abstracts for 1917 numbered 2,858 and occupied 1,308 pages. The great decrease in the number of memoirs in journals devoted to chemistry and allied subjects referred to in the Reports for 1916 and 1917 became, as was expected, still more marked in 1918; there is, however, some slight reason to hope that the lowest point has been reached, and that an increase in the number of papers abstracted may now be anticipated. Whilst most of the Continental journals have been obtained for abstraction, no Russian journals have come to hand during the year.

In the last Report, an account was given of the arrangements made by a Joint Committee of the Chemical Society and Society of Chemical Industry to minimise duplication in the abstracts published in the Journals of the two Societies. This arrangement has been in force during the year with satisfactory results.

The abstracts may be classified as follows:

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	—	771
Physiological Chemistry	—	237
Chemistry of Vegetable Physiology and Agriculture	—	160
	564	1,168
PART II.		
General and Physical Chemistry	—	557
Inorganic Chemistry	—	205
Mineralogical Chemistry	—	59
Analytical Chemistry	—	447
	468	1,268
Total in Parts I. and II	1,032	2,436

The scheme for supplying the abstracts of the Chemical Society and of the Society of Chemical Industry to the members of both Societies has been further considered, but owing to many difficulties arising out of the war, such as the greatly increased cost of production, it has been postponed for the present.

The Report on the progress of Radioactivity for 1917, which was omitted from the last volume of Annual Reports, is included with that for 1918 in the current Volume XV; it has been decided to postpone the Report on Crystallography and Mineralogy for 1918 and to combine this with the Report for 1919. Permission has been given for the publication of a French translation of Volume XV of the Annual Reports.

The publication of the List of Fellows has been resumed, but, owing to the need for economy, the list has been issued only to those Fellows who made application.

Following the scheme initiated three years ago, arrangements have been made for the delivery of Lectures to the Society during the present session. The first, entitled "The conception of the chemical element as enlarged by the study of radioactive change," was given by Professor F. Soddy on December 19th; on March 6th a lecture on "Emission spectra and atomic structure" was delivered by Professor Nicholson, whilst Professor Jeans will give a lecture on May 1st dealing with "The quantum theory and new theories of atomic structure."

The address delivered by the President at the last Annual Meeting was, by order of the Council, widely circulated throughout the country. The emphasis laid in this address on the desirability of closer co-operation between the societies representing the various branches of chemistry has given rise to a definite step in this direction by the promotion of "The Federal Council for Pure and Applied Chemistry." The Federal Council consists of representatives appointed by the following eleven societies: the Chemical Society, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Institute of Chemistry, the Society of Public Analysts, the Faraday Society, the Biochemical Society, the Iron and Steel Institute, the Institute of Brewing, the Society of Dyers and Colourists, and the Society of Glass Technology. The delegates elected by the Council to represent the Society on this body are Professor H. E. Armstrong, Sir William J. Pope, and Sir William A. Tilden. The primary objects of the new body are to consider and act upon all matters involving the common interests of the constituent societies and to deal with any question which these may place before it. The provision of a House adequate to the requirements of the chemical profession, in

which a complete scientific and technical Library could b assembled, is now under the consideration of the Federal Council.

The Council have had under consideration the present condition of chemical research, and they have given particular attention t the question of the adequacy of the sums available for grants an to the restricted supply of pure chemicals. Since it appeare desirable that united action should be taken in these matters, th Federal Council has been requested to consider them, and ha already taken action in both directions.

The demobilisation of chemists has also had the earnest atter tion of the Council, and joint representation with the Roy Society, the Institute of Chemistry, and the Chemical Warfar Department has been made to the proper authorities.

The Council have recently received a valuable report from th General Committee of Chemical and Allied Societies on the pr posed publication of chemical compendia in the English languag The report has also been placed before the Federal Council an the councils of other interested societies, including those of th American and French Chemical Societies, with the view of securin their co-operation.

During the past year a Committee has been appointed to con sider what changes it is desirable to make in the Bye-laws of th Society. In their report, the Committee have recommended con siderable changes, but these are in several respects inconsistent wit the terms of the present Charter, and therefore cannot be mac until a supplemental Charter has been obtained. The questic whether application for a supplemental Charter should be mac will shortly be laid before an Extraordinary General Meeting.

Sir William A. Tilden represented the Society on the Section Committee of the British Scientific Products Exhibition.

Professor P. F. Frankland and Dr. A. Scott continue to act the Society's representatives on the Conjoint Board of Scienti Societies, whilst Sir William J. Pope has been appointed a delega to the International Association of Chemical Societies in place the late Sir William Ramsay.

The Council are glad to report that, as a result of the Confe ence of Chemical and Allied Societies, a scheme has been prepar and is now in operation for increasing the use of the Library a extending its technical equipment. The co-operation and financi assistance of the Association of British Chemical Manufacture the Biochemical Society, the Faraday Society, the Institute Chemistry, the Society of Chemical Industry, the Society of Dye and Colourists, and the Society of Public Analysts have be obtained. The members of these societies are now able to use t

Library on the same terms as Fellows, and their representatives have been added to the Library Committee.

As already announced, the Library is now open to 9 p.m. on Tuesdays and Fridays and to 5 o'clock on Saturdays, in addition to those evenings on which the Society meets.

The number of books borrowed from the Library during 1918 was 2,905, as against 2,157 in the previous year and 1,610 in 1916. The additions to the Library comprise 126 books, 255 volumes of periodicals, and 31 pamphlets, compared with 155 books, 282 volumes of periodicals, and 54 pamphlets in 1917.

The Council have the pleasure to report that a valuable gift of handsomely bound volumes of periodicals and systematic works has been received as a bequest from the late Mr. Sydney Lupton.

The accounts for the year 1918 show a balance of income over expenditure amounting to £2,489 4*s*. 4*d*., as against £1,652 9*s*. 11*d*. reported last March for the previous year. Whilst the income from all sources has been £10,082 14*s*. 11*d*., and is thus greater than that recorded for 1917 by £1,552 16*s*. 0*d*., the expenditure has exceeded that of 1917 by £716 1*s*. 7*d*., reaching the sum of £7,593 10*s*. 7*d*. Thus, although the increased expenditure exceeds the similar increase on the outlay for 1916, indicated by the Report of last year, it has been amply covered by the larger revenue.

The latter factor is composed of additional life compositions, £102, and admission fees, £352, whilst the subscriptions account reveals an improvement by £381 10*s*. 0*d*. To these are added increases of £89 12*s*. 7*d*. from interest on investments, £262 9*s*. 10*d*. from the sale of publications, and £92 15*s*. 11*d*. from advertisements in the Journal, although the net gain to the Society from this source is only £32 5*s*. 4*d*., owing to increased cost of printing. Donations to the Library amounting to £280 5*s*. 0*d*., and not having a corresponding reference in the Report for 1917, cannot properly be regarded as increased revenue, as more than this sum will be expended by the Society during the current year in augmenting the usefulness of the Library to members of the subscribing bodies.

As was anticipated from the conditions prevailing during 1918, expenses in producing the various publications have been greater than the corresponding costs for 1917, the total increase being £390 19*s*. 7*d*., of which £128 5*s*. 2*d*. is due to the list of Fellows, a publication suspended in 1917. The fact that this compilation cost £73 1*s*. 6*d*. in 1914, £73 6*s*. 7*d*. in 1915, and £73 16*s*. 4*d*. in 1916 throws an interesting light on the increase in printing charges and on the period of the War at which this became acute.

Administrative expenditure has also increased from £1,472 4*s*. 5*d*.

to £1,681 6*s.* 5*d.*, the principal items on this account being £161 14*s.* 10*d.* in staff salaries and war bonus, whilst miscellaneous printing, stationery, and postages have together increased by £85 18*s.* 8*d.* On the other hand, the exceptional outlay in library furniture required in 1917 has not been repeated, and is reflected in a saving of £61 9*s.* 9*d.* in the year under review.

The War has continued to affect the volume of Transactions and Abstracts, as indicated by the following synopsis:

	Number of Pages.		
	Trans.	Abstr.	Total.
1914	2,909	2,068	4,977
1915	1,862	1,944	3,806
1916	1,368	1,532	2,900
1917	1,128	1,308	2,436
1918	995	1,032	2,027

Nevertheless, the cost of printing the Journal has been £2,750 8*s.* 3*d.*, instead of £2,543 7*s.* 9*d.* in 1917, so that a reduction of 409 pages corresponds to an increase of £207 0*s.* 6*d.* in expenditure; this is owing to further appreciation in the cost of paper and to the necessity of raising the bonus paid to the printers, which now stands at 72½ per cent. on the pre-war rates.

£2,000 National War Bonds were purchased during the year, and the estimated value of the Society's other investments has improved by £414, so that, having regard to the fact that on December 31st, 1918, the cash account was about £420 higher than on the last day of 1917, the assets of the Society show an increase of £2,834, or a total increase of £3,640 if the Research Fund at its present estimated value is included.

The following grants have been made from the Research Fund during the year:

	£	s.	d.
Organic derivatives of bismuth. F. Challenger.	£15	0	0
An investigation of the phthalein series. M. Copisarow. ...	10	0	0
The velocity of reaction between the alkyl iodides and sodium methoxide. H. E. Cox.	10	0	0
Formation of heterocyclic ring systems by the condensation of chlorocarbamic esters and alcohols. R. L. Datta. ...	10	0	0
The action of alcohols on urea nitrate. P. K. Dutt. ...	5	0	0
Influence of the nitro-group on the mobility of the substituents in the benzene nucleus. J. Kenner. ...	5	0	0
The composition and structure of soaps. J. W. McBain. ...	15	0	0
Melting points of the substituted amides of the normal fatty acids. P. W. Robertson.	6	6	0
Synthesis of β-phenyl-β-hydroxymethylethylamine from cinnamic acid or ethyl cinnamate. E. H. Todd.	10	0	0
The space formulæ of diphenyl and its derivatives (continued). E. E. Turner.	10	0	0
Total	£96	6	0

	£ s. d.	£ s. d.
To Subscriptions received in advance	234 0 0	
	1 10 0	235 10 0
,, Sundry Creditors		841 5 4
,, Research Fund:—		
As per last Balance Sheet	14357 3 4	
Add Excess of Income over Expenditure for the year	539 13 9	
		14896 17 1
Chemical Society: Excess of Assets over Liabilities:—		
As per last Balance Sheet...	24758 7 5	
Add Excess of Income over Expenditure for the year	2489 4 4	
		27247 11 9
		£43221 4 2

Assets.

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212 8 6	
£1050 London and North Western Railway 3 per cent. Debenture Stock	839 12 0	
£1520 14*s.* 8*d.* Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent. Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0	
£4941 Midland Railway 2½ per cent. Preference Stock	3572 2 5	
£1200 Leeds Corporation 3 per cent. Debenture Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460 13 6	
£1200 North British Railway 3 per cent. Debenture Stock	1033 11 0	
£700 Canada 3½ per cent. Stock, 1930/50	704 8 6	
£2100 5 per cent. War Stock } £3100 5 per cent. War Bonds }	5040 0 2	
(Estimated present value of Investments, £19,246 14*s.* 5*d.*)		26042 0 1
,, Sundry Debtors		1094 1 1
,, Subscriptions in Arrear Estimated to realise...		400 0 0
,, Insurance paid in advance		58 2 1
,, Cash at Bank—Deposit Account	300 0 0	
,, Current Account	353 9 0	
,, Cash in hand	16 14 10	
		670 3 10
,, Research Fund:—		
Investments (value when acquired):		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587 18 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049 15 11	
£1142 16*s.* New South Wales 3 per cent. Stock ...	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
£1365 Midland Railway 2½ per cent. Debenture Stock	1010 0 9	
£806 Victoria 3 per cent. Stock	706 6 2	
£4498 11*s.* 0*d.* 5 per cent. War Stock	4267 4 10	
(Estimated present value of Research Fund Investments. £12,013 15*s.* 8*d.*)		14634 2 5
,, Cash at Bank...		262 14 3
		£43221 4 2

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, Queen Victoria Street, E.C.
March 5th, 1919.

Approved—C. F. CROSS.
GEORGE SENTER,
ARTHUR R. LING.

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions				349	0	0
,, Admission Fees				956	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1918	139	3	4			
,, during 1918 ,, ,, ...	4729	16	8			
,, ,, ,, ,, 1917	392	0	0			
,, ,, ,, ,, 1916 and previous	62	0	0			
	5323	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	400	0	0			
	4923	0	0			
Add Arrears at date: 1918, £670; 1917 and previous, £524, estimated to realise as per Balance Sheet	460	0	0			
				5383	0	0
,, Lady Subscribers				9	8	9
Investments:—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...	170	15	8			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock	23	4	7			
,, £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...	33	1	6			
,, £1400 India 2½ per cent. Stock	25	7	6			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	42	0	0			
,, £4941 Midland Railway 2½ per cent. Preference Stock	79	7	2			
,, £1200 Leeds Corporation 3 per cent. Debenture Stock...	26	2	0			
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	31	10	0			
,, £1200 North British Railway 3 per cent. Debenture Stock	25	13	1			
,, £700 Canada 3½ per cent. Stock 1930/50	20	6	0			
,, £5200 5 per cent. War Stock and War Bonds...	205	8	3			
,, Income Tax Recovered	170	0	1			
,, Interest on Deposit Account	27	7	2			
				880	8	0
,, Publication Sales:—						
Journals	1728	6	0			
Proceedings	2	4	6			
Collective Index	33	17	2			
Library Catalogue	1	1	9			
Atomic Weight Tables		10	6			
Annual Reports on Progress of Chemistry	245	9	6			
Memorial Lectures	3	1	1			
Jubilee Volumes	0	17	6			
	2015	8	0			
Less Publishers' Commission	194	12	11			
				1820	15	
,, Proceeds of Advertisements in Journal...	£403	8	0			
Less Commission	29	8	4			
				373	19	
,, Miscellaneous Receipts				8	6	
,, Subscriptions from other Societies				22	1	
Donations to Library				280	5	
				£10,083	14	

FOR THE YEAR ENDED 31ST DECEMBER, 1918.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal :—						
Salary of Editor, including Indexing ...	620	0	0			
Salary of Sub-Editor and Assistant ...	250	0	0			
Editorial Postages ...	21	18	5			
Abstractors' Fees ...	240	12	1			
Printing of Journal ...	2750	8	3			
Binding ...	82	2	6			
Printing of Advertisements ...	164	13	2			
Wrappers and Addressing ...	4	5	4			
Distribution of Journal ...	398	19	4			
Authors' Copies ...	111	11	1			
Insurance of Stock ...	14	11	8			
				4659	1	10
" Annual Reports on the Progress of Chemistry ...				460	4	9
" Purchase of back numbers of Journal ...				6	4	3
" List of Fellows ...				128	5	2
" Library Expenses :—						
Salary of Librarian and Assistant...	371	17	0			
Books and Periodicals ...	199	1	8			
Binding ...	42	4	6			
				613	3	2
" Indexing for International Catalogue ...				30	0	0
" Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological ...				10	0	0
" Donation to Board of Scientific Societies...				5	5	0
" Administrative Expenses :—						
Salary of Staff ...	539	15	0			
War Bonus ...	254	6	7			
Wages (Commissionaire, Housekeeper, and Charwoman) ...	215	19	0			
Coal and Lighting ...	61	18	1			
House Expenses and Repairs ...	87	2	4			
Furniture ...	8	3	0			
Tea Expenses ...	35	3	3			
Insurances ...	39	6	6			
Accountants' Charges ...	21	0	0			
Commission on Recovery of Income Tax ...	8	10	0			
Law Costs ...	10	10	0			
Miscellaneous Printing ...	129	4	6			
Stationery ...	129	17	4			
Postages...	105	19	8			
Miscellaneous Expenses ...	31	11	2			
				1681	6	5
Balance, being excess of Income over Expenditure carried to Balance Sheet ...				2189	4	4
				£10,082	14	11

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1918.

Income.	£ s. d.	£ s. d.
To Dividends on:—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	29 10 6	
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	111 13 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	19 1 3	
£1142 16s. New South Wales 3 per cent. Stock...	24 17 2	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	24 11 5	
£1365 Midland Railway 2½ per cent. Debenture Stock ...	25 3 4	
£806 Victoria 3 per cent. Stock	17 10 7	
£4498 11s. 0d. 5 per cent. War Loan	217 0 0	
		469 7 3
,, Repayment of Cost of Apparatus		7 12 0
,, Repayments of Research-Grants		81 10 1
,, Income Tax Recovered		106 19 11
		£665 9 3

Expenditure.	£ s. d.
By Grants	96 6 0
,, Bankers' Charges	2 6
,, Commission on Recovery of Income Tax	5 7 0
,, Advertisements	2 0 0
,, Longstaff Medal	2 0 0
,, Do. do. Grant to Medallist	20 0 0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet	539 13 9
	£665 9 3

Although one disbursement (£10) only was made in 1917, the balance of income over expenditure for 1918 is £539 13*s*. 9*d*., as against £553 2*s*. 0*d*. for the previous year. This is explained by an increase of £50 11*s*. 3*d*. in the proceeds from investments, of £20 8*s*. 3*d*. in repayments of research grants, and of £14 0*s*. 3*d*. in the amount of income-tax recovered. £816 19*s*. 9*d*. Five Per Cent. War Loan was purchased for this account during 1918.

A vote of thanks to the Auditors proposed by the TREASURER was seconded by Mr. R. G. DURRANT, Dr. G. SENTER making acknowledgment.

On the motion of Mr. W. BARLOW, seconded by Mr. W. F. REID, a vote of thanks was proposed to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. Acknowledgment was made by Dr. F. L. PYMAN.

The ballot was then declared closed.

The PRESIDENT delivered his Address, entitled "Chemistry in the National Service." A vote of thanks to the President for his services in the Chair and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions, was moved by Professor H. E. ARMSTRONG. Col. C. T. HEYCOCK seconded the motion, which was carried with acclamation, the PRESIDENT making brief acknowledgment.

The report of the Scrutators was presented, and the PRESIDENT announced that the following had been elected as Officers and Council for the ensuing year:

President.—Sir James Johnston Dobbie, M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, C.B.E., M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Frederick George Donnan, M.A., Ph.D., F.R.S.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Arthur Smithells, C.M.G., F.R.S.; James Walker, D.Sc., LL.D., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries.—Samuel Smiles, O.B.E., D.Sc., F.R.S.; James Charles Philip, O.B.E., M.A., D.Sc., Ph.D.

Foreign Secretary.—Arthur William Crossley, C.M.G., D.Sc., F.R.S.

Ordinary Members of Council.—Julian Levett Baker; Alexander Findlay, M.A., D.Sc., Ph.D.; Francis Ernest Francis, D.Sc., Ph.D.; John Addyman Gardner, M.A.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Anderson Henry, D.Sc.; Charles Alexander Hill, B.Sc.; James Colquhoun Irvine, D.Sc., Ph.D., F.R.S.; Charles Alexander Keane, D.Sc., Ph.D.; Robert Howson Pickard, D.Sc., Ph.D., F.R.S.; Sir Robert Robertson, K.B.E., M.A., D.Sc., F.R.S.; Edward William Voelcker.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 27th, 1919.

By SIR WILLIAM J. POPE, K.B.E., F.R.S.

Chemistry in the National Service.

SINCE the autumn of 1914 a great change has taken place in the public attitude towards the natural sciences, and towards chemistry in particular. One of the recognised duties of the spokesmen of science during the past sixty years or more has been that of endeavouring to bring home to the general public and to its administrators the danger of neglecting the cultivation of pure and applied science. The eloquent discourses of our predecessors, Lyon Playfair, Roscoe, Meldola, and the veterans happily still with us, Tilden and Armstrong, all past-presidents of our society, on the national importance of chemistry, are well known to all of us, but we cannot claim that these utterances produced an effect compatible with their gravity.

Recent events have, however, given a stimulus to the popular appreciation of the need for wider application to scientific investigation of all kinds, which is incomparably greater than had been excited by the previous half-century of the spoken and written word. It may be useful at the present time to consider a few of the causes for this change in public opinion, partly because of the clarification of ideas which emerges from free discussion, partly because of the desirability of recording certain facts and particulars which may be of value to future historians of the strenuous period now ending and giving place to another still more strenuous.

At this time four years ago an urgent call was made for the services in a military capacity of all the chemists who could be spared from civil life. Large numbers were taken into the Army and formed the nucleus of the magnificent Gas Warfare Service, which has been slowly but efficiently developed. Many of these colleagues of ours are now returning to their legitimate spheres in the industrial and scientific life of the Empire, but many will not return; among those who have fallen I would refer more particularly to one who is well known to most of us present for the

invaluable services which he rendered on the defensive side of chemical warfare. Lieut.-Colonel Harrison was one of the great discoveries of the War, and his death on the eve of the armistice was one of its many great tragedies; the protection against gas poisoning which has been employed by our own and allied troops, a protection far more efficient than that ensured by the devices elaborated at leisure by the Central Powers, was due mainly to his wide knowledge, great organising ability, and unfailing resourcefulness in emergency. A movement for the establishment of a memorial to Colonel Harrison was set on foot by the Chemical Warfare Committee, of which he was the Controller at the time of his death, and a considerable sum has been collected from those who had been associated with him in his work for the Services. The Chemical Warfare Committee have approached the Council of the Chemical Society, and have offered under certain conditions to place a memorial tablet or other suitable permanent memorial in these rooms, and also to establish, under certain further conditions, a trust fund to be held by the Society. The Council have with great pleasure intimated their willingness to accept these gifts, and one of the first duties of your new Council will be to decide how best to carry out the provisions of the trust deed.

The efficiency of the British gas protection, which called for the exhibition of so much scientific skill both in research and in manufacture, and led to its adoption by our Allies, is one striking illustration of the paramount importance of science which has appealed to the general public. This subject is, however, but a small branch of the enormous chemical problem which presented itself to the nation nearly five years ago and led to the organisation under Lord Moulton of the Department of Explosives Supplies. During the working out of this problem, issues presented themselves which are probably dissimilar from any that have ever arisen before.

Thus, as the magnitude of the struggle became gradually obvious, it was realised that the whole of the resources of the Empire would have to be utilised fully if success was to be attained. A census of all available chemical products had to be taken, and schemes for their exploitation laid down; all materials had to be apportioned out in accordance with the principle that whatever was used for the manufacture of one particular war material left a corresponding shortage of raw material in connexion with the manufacture of some other, and perhaps equally essential, product. The intricacy of gauging the chlorine output of the country, of determining how to increase it at the maximum rate without unduly disturbing other interests, of apportioning it

most advantageously for use as liquid chlorine and for the manufacture of phosgene, sulphur chloride, carbon tetrachloride, bleaching powder, and many other war materials, is such as would disarm criticism even if the result had been failure instead of brilliant success. This novel mode of presentment, involving recognition of the principle that the Empire could only dispose of certain limited and measurable quantities of raw materials, was but one of many fresh views which forced themselves upon a newly created Ministerial Department. Labour, fuel, and transport had to be discussed in an analogous manner.

The cessation of hostilities found this country manufacturing, roughly, 100,000 tons per annum of nitric acid and sulphur trioxide, with an efficiency of about 93 and 91 per cent. respectively of that theoretically obtainable; we were also making 60,000 tons of T.N.T. and 35,000 tons of cordite per annum. These productions were for all practical purposes on a permanent basis, and could have been continued indefinitely. The factories necessary for securing this huge production were erected by the Government, and for several reasons. First, for economy in production. In spite of the large initial cost of installation, and including rapid amortisation, the national production of cordite was better in quality than, and of approximately one-half the cost of, that imported from America. Secondly, for certainty of supply, which could be ensured only by a home production not subject to the risks of oversea transport.

With this necessity for gigantic production, the urgency for economy in manufacture necessarily went hand in hand. One of the most interesting documents of the war is the second report on costs and efficiencies for H.M. factories controlled by the Department of Explosives Supplies, which has been recently issued. This report contains a minute analysis of the working costs for each period of each factory engaged on individual items of manufacture; it states what proportion of the cost per ton of product is borne by labour, raw materials, fuel, maintenance, etc., and provides an incitement to further effort towards economy of working by giving a "bogey" cost sheet made up of the most efficient details of cost selected from the complete analysis of expenses. It will be clear that an immense amount of organising power was required to achieve this stupendous result; it was due largely to the genius and energy of Mr. K. B. Quinan.

It must be remembered, however, that this permanent memorial to British chemical activity in production was rendered possible only by the intense effort of the army of chemists and engineers enlisted under the command of Lord Moulton. The necessity for

utilising all the chemical resources of the country to the utmost led, in direct relationship with the census of raw materials previously mentioned, to the attempt to extract the last possible fraction of efficiency in each component process. The huge production just indicated made it very profitable to carry out a vast amount of careful scientific investigation of details of manufacture; so many Fellows of this Society devoted their best efforts to this work that it would be invidious to mention names. Our colleagues have had ample opportunity to realise that the romance of war is now to be found in the laboratory, the workshop, and the factory quite as much as on the battlefield.

An instructive example of the operations of the struggle for economy in the production of a given effect is found in the rivalry which arose between picric acid and ammonium nitrate for use as high explosives. Picric acid costs about £185 per ton to make, ammonium nitrate about £50, and T.N.T. about £100 per ton; the high cost of picric acid means, of course, limited production. A mixture of 80 parts of ammonium nitrate with 20 parts of T.N.T., known as amatol, was introduced early by the Research Department at Woolwich, as being about 5 per cent. more powerful as a high explosive, less "brisant," and more difficult to detonate, and, of course, far less costly to manufacture. The course of the war has been marked by continued progress at the hands of our research chemists in the preparation and applications of amatol; the growing appreciation of the merits of this material led to the discontinuance of the manufacture of picric acid in this country last summer, to the adoption of amatol in place of picric acid as the American standard high explosive, to the approaching elimination of picric acid from the Italian military programme, and to the replacement, in the main, of picric acid by amatol in the French service.

A very pertinent question arises in connexion with the fact that our production of the chemical materials needed for a great European war was negligibly small in 1914 and has gradually attained satisfactory dimensions. We know that the great chemical factories of Central Europe could divert their peace production of chemical products to a war output at very short notice. None of these huge installations requires much time for the design and construction of chemical plant for new purposes; all possess a series of standard items of equipment which can be fitted together rapidly to form a piece of plant capable of use for throwing any ordinary laboratory operation into large-scale practice. Stills, condensers, pressure vessels, filter presses, cooling arrangements of coils and

he like, are available in standard sizes and with standard fittings n such a manner that the installation on a works scale of a laboratory operation is deprived of its most formidable difficulties. The question which demands an answer is why, when the German works were in existence and could attain a war production so quickly, were the Allied nations given time to gradually develop their war production of explosives, noxious materials, etc., from nothing? The question is best answered by an example.

In July, 1917, the Germans first used against the Allies a new offensive material, $\beta\beta$-dichloroethyl sulphide, $(CH_2Cl{\cdot}CH_2)_2S$, and with very great success. This substance, the so-called "mustard gas," has but little odour, and exposure to it causes comparatively few fatalities; inhalation of, or contact with, its vapour gives rise to acute pneumonia, to the production of painful sores, and to temporary or even permanent blindness. Whilst, as has been stated, the actual mortality is low, and the use of the substance may to this extent be described as humane, the casualties produced are very numerous; slight exposure to a material so toxic and so difficult to detect leads, in general, to six weeks in hospital. The preparation of $\beta\beta$-dichloroethyl sulphide was described by Victor Meyer in 1886, and involved the several operations indicated by the following set of equations:

(1) $CH_2{:}CH_2 + HClO = CH_2Cl{\cdot}CH_2{\cdot}OH$.

(2) $2CH_2Cl{\cdot}CH_2{\cdot}OH + Na_2S = (HO{\cdot}CH_2{\cdot}CH_2)_2S + 2NaCl$.

(3) $(HO{\cdot}CH_2{\cdot}CH_2)_2S + 2HCl = (CH_2Cl{\cdot}CH_2)_2S + 2H_2O$.

When it is realised that operation No. 1 is difficult and that the products of reactions (1) and (2) are soluble in water, it will be understood that no small difficulties must present themselves in the manufacture of $\beta\beta$-dichloroethyl sulphide by this process on a large scale. The examination of the German product made it quite clear, however, that the process of manufacture adopted was that indicated by the above set of equations; the over-all yield of product is perhaps 40 to 60 per cent. of the theoretical. In view of the difficulties of manufacture, it was fairly certain that no chemical installation for its production could be established under the control of the Allies within any reasonable time; the Central Nations thus supposed that they held the monopoly of a very powerful instrument of war.

Most British organic chemists were, I think, amazed at the method of production adopted by the German manufacturers; to apply such a technically cumbrous process for the manufacture of so simple a compound seemed quite irrational. By the end of

January, 1918, a process for making $\beta\beta$-dichloroethyl sulphide had been worked out in the British laboratories, which consisted of the reaction expressed by the following equation:

$$2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2S + S;$$

the yield obtained in the laboratory was 98 to 99 per cent. of that theoretically possible. The new method was communicated to France and America, and installed by the three Great Allies on a large scale; at the conclusion of the armistice the available daily production of mustard gas by the Allies was equal to the monthly production of the Central Nations.

The answer to the question just put is now available. The German chemical service was inefficient; the scientific chemists under its control were incompetent.

The Allied production of mustard gas had a potentiality of the order of thirty times as great as that of the German; the cost of the German material was of the order of thirty times as great as that of our product. Cost of production under the conditions prevailing for this particular material means, in the end, expenditure in labour; that we were able to produce at something of the order of one-thirtieth of the cost of the German production means that by the allocation of the same quantity of raw materials we could secure thirty times the output. The relative strain on the productive resources of the Allies and the Central Nations caused by a demand for a certain quantity of "mustard gas" is measured roughly by the indicated ratio of one to thirty.

Whilst many instances similar to that of mustard gas might be quoted to show that Germany has been badly served by her scientific men during the war, it would be difficult to overrate the effects of the skill and perseverance exhibited by the German chemical manufacturer. The command of great and long-established factories for fine chemical manufacture enabled the German technologist to throw faulty academic projects rapidly into large-scale production; the cost, namely, the strain on national resources, was enormous, but that an output could have been achieved is a significant tribute to the potentialities represented by the large German fine chemical factories. Both in Britain and Germany production in chemical manufacture has been multiplied during the war, but necessarily in a different manner. Our large production is almost entirely of war importance, and most of the works installed during the war must now be dismantled as a result of the cessation of hostilities; the German expansions, on the other hand, constitute a permanent addition to the potentialities of peace manufacture of staple marketable products. The war has left Germany

with vastly increased resources as a manufacturer of much needed chemical products.

The view that our country is superior to Germany in the possession of creative scientific power has always been maintained in modern times by students of philosophy and history; the correctness of the view has been amply demonstrated during the last four years. Whilst our nation has overcome its initial handicap by a continuous flow of novel scientific devices of military value, our enemies passed through the war with little more in the shape of novel effects than those laboriously elaborated during the preceding years of peace. The more brilliant position which Germany has so long held in applied science arose from the keen appreciation exhibited by German public and official authorities of the rich economic fruits to be reaped from the systematic exploitation of scientific industry as compared with the neglect of scientific effort shown by corresponding classes in this country. Even yet, but small encouragement exists for those who desire to see pure and applied science flourish as it deserves in Great Britain; although it may be long before the scientific industries of Central Europe regain their former predominance, there seems but little prospect of sufficient official encouragement being given in this country to scientific and industrial initiative to ensure our position in the competition with other nations.

In this connexion it is interesting to notice what is happening in the United States. Immediately after her entry into the war America initiated a census of chemists, and in July, 1917, a fully detailed description was available of some 15,000 chemists resident in the States; a research staff consisting of 1200 technical men with appropriate assistance was enlisted for the Research Division of the Chemical Warfare Service alone. Since America was only in the war for about eighteen months this powerful organisation had not time to make its efforts properly felt. Apart from small improvements or changes in detail, practically all the American chemical equipment, both for offence and defence, was manufactured on the detailed plans furnished by Great Britain or France; the available time was too short to allow full play to American genius for novelty and for magnitude of production. The necessity for co-operation brought large numbers of young and active American chemical officers to Europe; it gave those officers for eighteen months the entry to practically every chemical works of importance in England and France, and unrivalled opportunities for accurately judging European chemical methods and markets. These men have now returned to their ordinary scientific and technical pursuits in the States, and it cannot be expected that they have left behind them

the unique experience which they have gained of European conditions.

We may anticipate that competition in pure and applied chemistry between Europe and America will become increasingly keener during the years to come. The competition is already intense, and gives little promise as yet of turning in our favour; it is, in fact, difficult to see how many of the staple products of fine chemical manufacture can hold their own in Great Britain against American competition under the conditions which arose during the first three years of the war. During these years peace production flourished in the States free from Government control, whilst in this country the establishment of a fine chemical industry in war time was naturally rendered far more difficult by State control of works, materials, and labour. The bearing of this may be made clear by an instance. The manufacture of "saccharin" was installed in England after the outbreak of war, but the production was controlled in that the manufacturers were only permitted to sell at a profit of 10 per cent. on the cost, this profit being, in turn, subject to the excess profits tax; further, to prevent the economic difficulties which were foreseen if "saccharin" competed with sugar, the price of English-made "saccharin" was fixed at a figure which involved the very large addition of thirty shillings per pound to the price, this addition being appropriated by the Government. Simultaneously, "saccharin" was manufactured free of all control in the States; it came into this country unrestricted and on such terms that the American producer took the thirty shillings per pound just mentioned in addition to the considerable profit previously made by reason of lower cost of manufacture. America having thus been assisted by our Government to build up a large reserve of profits, is now actually selling "saccharin" in England at eleven shillings per pound—a price at which it cannot be produced here—apparently with the legitimate trade purpose of destroying the English manufacture and subsequently running up the price.

Many cases may be quoted as closely analogous to that of "saccharin," notably in connexion with acetic acid, glycerol, acetone, and methyl alcohol and their products, in which British procedure has facilitated profiteering in foreign countries during the war. The excess profits tax operated insidiously in tempting British manufacturers to keep prices high so as to retain a margin with which to write off capital expenditure in spite of the tax; the foreign competitor, free from Government control of raw materials and exempt from the excess profits tax, was able to take full advantage of the ruling high rates. It will be of interest to see how the problems introduced by these actual occurrences are to be solved advantage-

ously for Great Britain in the great reconstruction upon which our administrators are now engaged.

Sufficient has probably now been said in justification of the rapid appreciation of science, and especially of that branch of science with which we are particularly concerned, in the public and administrative eye. The sudden incidence of new scientific modes of military and naval attack and the quick improvisation and development of equally scientific means of reply, both of which have been so frequently exhibited during the past five years, must have seemed uncanny to the lay observer, who only realised the effects but did not understand the causes.

At the present time, however, most Fellows of this Society have little leisure to reflect on the ghastly tragedy in which it has been our privilege to assist; the curtain has fallen upon this, but is rising again on the greatest epoch in the history of the world. The coming struggle for scientific and industrial position, on the results of which must rest the whole intellectual, artistic, and material future of our race, will call for longer, greater, more persistent and more intelligent effort than any which we have hitherto exerted. We are forced to consider whether we have reason to hope that the recent lessons have been well brought home and whether the free play given to scientific creation and production during the last five years is to persist unhampered in the future. For purposes of war our administrators gave every incentive to scientific investigation; money, men, and material were provided for the asking, free from Treasury control, free, in fact, from all control other than that of the scientific worker able and willing to organise and execute a necessary piece of work.

I see no reason to think that the lesson has been properly learnt and every reason to anticipate a re-establishment of that parsimonious treatment of scientific effort which seems now to belong to a past age, but with which we were all well acquainted five years ago. The control of scientific research is again leaving the hands of the scientific man and being resumed by the lay administrator. The old remark has been resuscitated quite recently that "it is a common-place among administrators to fear the expert." The non-technical administrator has no means of distinguishing the expert from the charlatan; he has perforce to regard the scientific expert as the lineal descendant of the "adept" of alchemical times whose claim to recollection is based upon the adroitness with which he was able to divert public funds to his own base purposes.

It is quite clear that if scientific research is to be assisted by the State—and unless so aided it will languish and carry with it into decadence every activity of the Empire—it must be adminis-

tered by men of scientific training and eminence; any other mode of procedure will necessarily lead to the strangulation of scientific effort by departmental red-tape. In this connexion it is again instructive to refer to American practise; our blood-relatives across the Atlantic had three years in which to study in peace the efforts which we were making in war, and it cannot but be useful to observe the manner in which they propose to profit by our experience.

In 1916, President Wilson, a University professor and an expert, now one of the most imposing figures in terrestrial affairs, called upon the National Academy of Sciences at Washington to nominate the members of a "National Research Council"; the object of this new organisation was stated to be that of co-ordinating the scientific work of the country in order that the scientific problems both of war and of peace might be more efficiently solved. The National Research Council is under the presidency of one of the most eminent among the active American men of science, Professor George E. Hale, of the Mount Wilson Observatory, and has large funds at its command for research purposes. Two points are conspicuous in connexion with the American programme: first, the substitution of the professional lay administrator by the ordinary office staff; secondly, the recognition of the close interdependence of pure and applied science. The contention which has long been advanced in this country, that an adequate output of purely academic chemical research work and the existence of a flourishing fine chemical industry are mutually essential, is here tacitly accepted; the former seeks in the industries remunerative positions for the products of its training, and the fine chemical industry looks to the scientific investigator for inspiration and new directions for enterprise. The nation which possesses an extensive organic chemical industry controls chemical warfare, the production of pharmaceutical and photographic products, the textile industry, and many other great departments of human activity.

The operations of the great American organisation for the stimulation of scientific research work are already making themselves felt. They have produced just recently an entirely novel method for oxidising naphthalene to phthalic acid, presumably by the use of atmospheric oxygen and a catalyst, which gives a 95 per cent. yield, and are responsible for the huge nitrogen fixation scheme now under installation in the States. These two illustrations alone, the one small and the other large, leave us in no doubt as to the influence which the National Research Council is destined to exert on scientific and technical progress throughout the world.

If British science is to make itself adequately felt in the great

intellectual and material advances of the near future, British men of science must be entrusted with the initiative power and the command of money which they have enjoyed during the past few years; unless this is done our Empire will, as before, continue to fall behind other great nations as a contributor to the increasing mass of pure and applied scientific knowledge.

In an address which I had the honour of delivering in this room a year ago attention was called to the necessity for closer co-operation between the large Societies representing the various chemical interests in Great Britain. During the past year action has been taken in this matter, and some fifteen of the Societies have collaborated in the establishment of a Federal Council for Pure and Applied Chemistry, the functions of which is to advance, safeguard, and voice the interests of chemical science. The Federal Council consists of representatives nominated by the component bodies, and is already occupying itself actively with the questions within its purview; it has moved with some success in connexion with the claims of experimental science to recognition in the recently established scheme for education within the Army, with the provision of fine chemicals for research purposes, with the remuneration of scientific posts, and with other matters. The Federal Council will continue to apply itself to those questions which are of importance to chemists as a class leaving more specific chemical interests to be dealt with by the appropriate constituent societies. A very similar project for the consolidation of the larger chemical interests is in course of execution by our French colleagues.

It is beyond question that a central house for accommodating the chemical societies in a manner more proportionate to their importance than is at present possible should be provided, that a common chemical library far more complete than any now available in this country should be at our service, and that some comprehensive scheme for the publication of compendia of chemical knowledge should be put into operation. A very imposing and costly programme confronts the recent amalgamation of chemical interests, but the universal approval which greeted the proposition for creating a Federal Council for Pure and Applied Chemistry is a happy augury for the future usefulness of the new organisation.

OBITUARY NOTICES.

JOHN PERCY BATEY.

Born March 22nd, 1889; Killed in Action April 9th, 1918.

John Percy Batey, M.Sc.(Tech.), was educated at the Manchester Municipal Secondary School, where he was awarded a three years' scholarship to the Manchester School of Technology. He took the degree of B.Sc.(Tech.) in 1908 when nineteen years of age, and was also awarded the Schuster Research Scholarship. Twelve months later he was made M.Sc.(Tech.). For a time he was lecturer and demonstrator, and in 1911 he became assistant to Dr. Liebmann, of Weybridge, where he remained until he enlisted in January, 1915.

He joined the Public Schools Battalion, the Middlesex Regiment, transferring later to the Royal Engineers, and went to France in August, 1915. He was promoted to the rank of Company Sergt.-Major in September, 1916. In 1917 he was awarded the Belgian Croix de Guerre, and in 1918 the D.C.M.

With regard to the D.C.M. the *Gazette* published the following:

"He volunteered on no less than eleven times in one month to conduct parties carrying rations and supplies over a very much exposed area that was being heavily shelled by the enemy to gun emplacements in the front line. The fine example of courage and devotion to duty of this warrant officer had an excellent effect on the N.C.O.'s and men of his company."

F. B.

LIEUT. CHARLES WILLIAM DICK.

Born April 10th, 1895; Died on Service November 9th, 1918.

Lieut. Charles William Dick, R.A.F., died of pneumonia on November 9th last in Cliff Military Hospital, Felixstowe. Mr. Dick, who was the younger son of the late Mr. J. Dick, schoolmaster, North Shields, took 1st Class Honours in his Inter B.Sc.(London) on leaving Rutherford College, Newcastle-on-Tyne, in June, 1912,

and in the autumn of the same year gained an open science scholarship at Cambridge University and became a scholar of Trinity Hall in the autumn of 1913. He passed his final for the B.Sc.(Lond.) in 1914, and on completing two years' residence he postponed further study to become a chemist at Messrs. Curtiss' and Harvey's explosives works at Cliffe, near Chatham, and whilst there was elected a Fellow in 1917. He joined the Meteorological Section of the R.N.V.R. in April, 1918, and after completing his training was appointed meteorological officer at Felixstowe Air Station, and on the creation of the R.A.F. was transferred to its establishment in August, 1918.

J. E. D.

JAMES HECTOR BARNES, D.Sc.

BORN 1879; DIED 1917.

"I AM sorry to say I have been in very poor health all the summer and had to take six weeks' leave in Kashmir this autumn; it was no holiday, however, for I spent four weeks of it in bed with an irregular pulse—the old story of India, malaria, and, the doctors say, overwork. I hope to come home next summer, for I do not think I can stand another Indian summer here without first having a rest in a decent climate. I shall look you up then, and I hope you will be kind and put me in the way of being useful while at home on leave as I really cannot idle about."

These extracts are from a letter dated November 30th, 1916, received from Hector Barnes. He did not come home, and his prophecy was fulfilled; he did not stand another Indian summer, but at the age of thirty-eight, in the fullness of his intellectual powers, with high hopes and with great opportunities opening before him, he died in India. It is difficult indeed to write any adequate record of the worth and work of such a man. The scientific work which he accomplished, had it been carried out in the most favourable environment, was such as any chemist might be proud to have to his name. But it was carried out under conditions which would only be met by a man of heroic temperament. Such a man Barnes in truth was.

In the plains of Northern India, at Lyallpur, a remote station, on land recently transformed from a sterile desert into a luxuriant agricultural colony by the marvellous system of Indian irrigation, Barnes betook himself in 1906. Born in 1879, he had received his scientific training at the University of Birmingham, where he

studied chemistry and physics under Professors Frankland and Poynting and graduated B.Sc. He had previously been apprenticed to Messrs. Southall and Barclay, pharmaceutical chemists, and the experience of the practical conditions of manufacturing operations which he there acquired no doubt added greatly to his equipment for the work that was in store for him. At Lyallpur he held the position of agricultural chemist to the Punjab Government and professor of chemistry in the Agricultural College, then at the stage of inception. He threw himself wholeheartedly into the work of designing the chemical laboratories, and in 1908 his responsibilities were increased by his appointment as Principal of the College. A year later the College was open for the reception of students. There was an immediate response, as there is to every new educational enterprise in India; but when it was found that the College was not, as it was expected to be, a certain path to Government service, the numbers fell with great rapidity and any belief that there was widespread zeal among neighbouring landowners for agricultural science could not be sustained. Barnes, however, had cherished no illusions, and he knew from the first that the foundation on which he must build was sound scientific research addressed as directly as possible to vital questions of Indian agriculture, and to this he and his colleagues bent their energies. It is not easy to give an idea of what that meant. The physical obstacles imposed by the climate and ever-recurrent sickness, the isolation from the scientific world and from the meagre supplies of apparatus anywhere available in India—these alone might daunt a strong man. Add thereto, only in a more intense form, what we have in England—Government officials in authority whose "humanisation" has precluded the slightest knowledge of what science is, what it does, and how it can be applied to do more—and it may be understood that it is only the very exceptional man who can succeed. This Barnes did in the most conspicuous degree. Standing in the laboratories at Lyallpur after some hours' journey from Lahore through great tracts of solitude and finding apparently all the resources of a European university science department and men busily engaged in employing the experimental methods of modern physical chemistry in the elucidation of fundamental problems in agriculture, the greatness of the achievement was very striking to the imagination. Within a stone's throw were the mud walls of an Indian village with its population living unchanged in the beliefs, the thoughts, the habits of life and work that belong to distant centuries of the past.

The chief lines of work on which Barnes was engaged were salt lands and their reclamation; seepage and the rising of ground water-

level under irrigation conditions; the sugar cane and the sugar industry in the Punjab; the intensity of solar radiation; the Kangra tea industry; the chemical aspect of weevil attacks upon wheat. It is to be feared that his published papers and records will give no adequate idea of the comprehensive plans which he had in his mind in relation to the elucidation of these problems. He talked of them eagerly and in the most interesting way, showing at once his sound knowledge of fundamental science and his appreciation of practical conditions. He had erected a workshop and turned out from it many of the fine tools required in his work, and his laboratory methods exhibited the play of great experimental skill and resource. Space does not admit of any extended account of these investigations, but a little more may be said of one of them. On his last visit to Lyallpur in 1914 the writer was taken by Barnes to Narwala. This spot is twelve miles distant from Lyallpur, and is, or was, infertile salt-land, that is, land which owing to triumph of evaporation over rainfall has become impregnated with a variety of salts, carbonates, chlorides, and sulphates, especially of sodium, calcium, and magnesium, evident as a crust of "white alkali" or "black alkali" upon the soil. This condition of soil has been the subject of much study in America, but Barnes believed that the work had "failed to prove useful and practical for want of a better knowledge of the scientific principles of the causes of sterility. If such causes had been first investigated time and money would have been saved, and in the end the *practical* result would, as it always does, justify the scientist." Accordingly, Barnes set himself to study as closely as possible the physical, chemical, and biological aspects of the problem. Having satisfied himself of the principles involved, he applied himself to the practical problem of redeeming the land at Narwala, and at the time of the visit referred to a tract of infertile land was being mole drilled. Leaving fields where the leisurely ryot was urging his bullock to pull the wooden plough and gently scratch the surface soil, one passed to the Narwala tract where a Yorkshire artisan was found in contest, doubly bitter to him by the futility of his native tongue, with native inaptitude in dealing with a steam-driven mechanical monster from Leeds. The plan was to mole drain the land and then irrigate out so much of the salts as was shown by Barnes's biological methods to be necessary. The results of this trial were extraordinarily successful, and it is scarcely possible to believe that the luxuriant crops (of which photographs afterwards arrived) can have been grown on what was just before the war a stricken desert. Barnes in the end estimated that the system of reclamation would pay between 300 and 400 per cent. on the capital outlay, and its general application would, of course, add

millions to the wealth of India. He was proposing also to apply the system to non-irrigated areas by the use of water pumped from the subsoil.

In 1914 Barnes married Nora, daughter of the late Colonel Francis Thomas Steven, Indian Army.

As soon as the war began he bestirred himself to bring into action all the scientific and material resources that India could supply, but it is impossible at present to quote his important observations on this subject.

Shortly before his death Barnes, not without some reluctance on his part, left Lyallpur to take up at Pusa the post of chief agricultural chemist to the Government of India. What he might have accomplished from there it is idle to conjecture, but the thought of it only deepens the sense of calamity both to India and to Science that surrounds his untimely death.

Barnes was every inch a man and an Englishman. When the writer first saw him he had just come from among his students in the playing fields and was in football attire, a splendid figure of a man, eager, resolute, honest, and kindly. He was beloved by his students and colleagues and respected by everyone. In summing up his qualities in our mind it is impossible not to be struck with the strength and number of endowments that are needed to produce the type of man who is to be the true pioneer of progress in India--endowment of body, mind, and spirit. Happily, such pioneers have been found in the past. They will long be needed in the future of India, and it is difficult to think of any better service to mankind than is open there to those who can bring themselves to the standards that ruled the life and work of Hector Barnes. At Lyallpur his portrait and an annual prize have been set up to preserve his memory, and shortly before his death he was made a Doctor of Science of his University of Birmingham. His work and influence will endure in many fields and many hearts.

A. S.

GEORGE CAREY FOSTER.

BORN 1835; DIED FEBRUARY 9TH, 1919.

IN the death of Professor Carey Foster in his eighty-fourth year on February 9th, there are many who will feel the loss of a kind and generous friend, to whose gentle sympathy and encouragement much of the happiness, as well as much of the success, of their own lives has been due. A man of extreme modesty and of high

if not commanding ability, Carey Foster had made few direct contributions to scientific literature; but the soundness of his judgment, his almost passionate love of exact knowledge, and his enthusiasm, earned the respect of all, and made his presence invaluable on the many committees of learned societies, the British Association, and the various university boards of which he became a member. An extreme diffidence and a nervous shyness that was not without a peculiar charm to those who came to know him well, as well as a hesitation to express a definite opinion on subjects on which he did not feel on the firmest ground, made it easy to undervalue the services he rendered to science and education during the course of a long and active life.

George Carey Foster was the only son of George Foster, a calico printer and a Justice of the Peace for Lancashire and the West Riding of Yorkshire, and was born at Sabden, in Lancashire, in 1835. After an early education at private schools, he entered as a student at University College, London, where his studies were at first mainly directed to chemistry. He graduated in Honours and with a prize in chemistry in his twentieth year, and acted for some years as chemical assistant to Professor Alexander Williamson, who had then occupied the Chair of Chemistry for six years, and a warm attachment and regard sprang up between the two men. He left England in 1858, and spent some years in study at the foreign Universities of Ghent, where he was a student under Auguste Kekulé, at Paris, and at Heidelberg.

At this time, however, while he continued his chemical studies, his interest became more and more directed to physical science, which was then assuming a position of increasing importance through the work of such men as Clausius, Lord Kelvin, and Clerk Maxwell, and it was natural that the refined accuracy of physical measurements and the readiness which they admitted of mathematical treatment should have presented a strong attraction to a man of his type of mind. The first evidence of his new interest was the appearance in 1863 of two articles on "Heat" in the first edition of Watts's "Dictionary of Chemistry." These articles, extending together to more than 150 pages of closely printed matter, formed an admirably concise and critical statement of the position of an important branch of science, and at once established Carey Foster's reputation as a clear thinker and able exponent of physics.

In the meantime, in 1862, Carey Foster had accepted an invitation to assume the duties of professor of natural philosophy at the Andersonian University, Glasgow, and, in 1865 he was encouraged by his friend and former teacher, Williamson, to

become a candidate for the vacant professorship of experimental physics at University College. His election was mainly due to the high reputation he had established as the author of the articles in Watts's Dictionary, and in October, 1865, he entered on his career at the London College, of which he was elected a fellow in 1867, and with which his name will always be associated. He resigned his professorship in 1898, at the age of sixty-three, but was recalled to act as principal of the college for a period of four years from 1900, during a critical time in its history. The last years of his life were spent in the quiet and refinement of a country life on a small estate at Rickmansworth, although, until quite near the end, he was always ready to place his services at the disposal of the educational causes that had been so near his heart in former times. He became a Justice of the Peace for Hertfordshire, and took an interest in politics, in which he was a supporter of the Liberal Party. Towards the end of 1917, after the death of his wife, he began to feel the weight of advancing years, but up to within two weeks of his death he was at work on manuscripts submitted to him for publication in the *Philosophical Magazine*. At the end of January of the present year he had a slight attack of congestion of the lungs, which his heart was not strong enough to resist, and, after gradually becoming weaker, he passed away in the presence of his children on February 9th.

Carey Foster's contributions to chemistry were published between 1857 and 1867. The writer, who is profoundly ignorant in chemical matters, is indebted to his friend, Dr. Forster Morley, for the following summary of these researches. Dr. Morley was engaged in several physical researches under the direction of Carey Foster while a student at University College, and was intimately acquainted with him during the remainder of his life.

"The first paper by Carey Foster appeared in the notes and abstracts appended to the British Association Reports for 1857. It is entitled 'On suggestions towards a more systematic nomenclature for organic bodies.' Gerhardt having introduced the term *homologous* to denote that two carbon compounds differed in their formulæ by CH_2 or a multiple thereof, Foster now proposed a new adjective, *isologous*, to indicate a difference of H_2 or a multiple of H_2. This adjective is still employed to denote the difference. He further suggested words composed of two Greek numerals, the first of which related to homology and the second to isology. Thus *deutritic* would mean 'belonging to the second homologous series and the third isologous series.' This suggestion, together with many other ingenious proposals for new nomenclature, did not receive support from other writers

"In 1859 Carey Foster presented a preliminary report to the British Association 'On the Recent Progress and Present State of Organic Chemistry' (*Rep. Brit. Assoc.*, 1859, 1). This was a review of recent work, particularly from the point of view of the development of ideas about formulæ.

"In the Chemical Society's Quarterly Journal (1860, **13**, 235) we find a paper 'On Acetoxybenzamic, an Isomer of Hippuric, Acid,' by G. C. Foster. It is dated Ghent, 1860, and is an account of a very careful piece of work carried out under the direction of Professor Kekulé, and describes the first preparation of *m*-acetylaminobenzoic acid, which is shown to be related to hippuric acid, from which it might, in imagination, be derived by an interchange between the radicles of benzoic and acetic acids.

"A paper published in 1861 'On Piperic and Hydropiperic Acids' appeared in the Chemical Society's *Journal* (1862, **15**, 17; also in *Rep. Brit. Assoc.*, 1861, 78, and *Annalen*, 1862, **124**, 115). In this it is shown that piperic acid, $C_{12}H_{10}O_4$, is reduced to hydropiperic acid, $C_{12}H_{12}O_4$, and a large number of the salts of the latter are described.

"The most important chemical work carried out by Carey Foster is contained in three papers published in conjunction with Matthiessen. The first is entitled 'Preliminary Notice of Researches into the Chemical Constitution of Narcotine,' and was read before the Royal Society in 1860 (*Proc. Roy. Soc.*, 1861, ii, 55; *Phil. Mag.*, 1861, [iv], **22**, 398). In this the authors establish the formula $C_{22}H_{23}O_7N$ for narcotine, and show that this alkaloid gives off methyl iodide when heated with hydriodic acid. The oxidation of narcotine to opianic acid is discussed, and the formula for opianic acid, $C_{10}H_{10}O_5$, correctly determined. It is also shown that, on heating with concentrated potash, opianic acid can be neatly split up into meconin and hemipic acid. A new acid, cotarnic acid, was obtained by the gentle oxidation of cotarnine.

"The second paper on this subject, entitled 'Researches into the Chemical Constitution of Narcotine and of its Products of Decomposition,' was published in 1863 (*Phil. Trans.*, 1863, 345; an abridgment is given in *J. Chem. Soc.*, 1863, **16**, 342). The authors here describe how, by acting on hemipic acid with hydriodic acid, an acid, $C_7H_6O_4$, which they call 'hypogallic acid,' but which is now known as protocatechuic acid, is obtained. As an intermediate product they isolated 'methylhypogallic acid,' now called '*iso*valeric acid.'

"The third paper is entitled 'Researches into the Chemical Constitution of Narcotine and its Products of Decomposition, Part II,' and was read before the Royal Society in 1867 (*Proc. Roy.*

Soc., **16**, 39; *J. Chem. Soc.*, 1868, **21**, 357). It is shown that opianic acid, when heated with hydrochloric or hydriodic acid, forms methyl chloride or iodide, and a new acid, 'methylnoropianic acid,' $C_9H_8O_5$. Thus, opianic acid may be called dimethyl-noropianic acid. Methylnoropianic acid yields with nitric acid nitromethylnoropianic acid. Meconin, on heating to 100° with concentrated hydrochloric or hydriodic acid, yields methyl chloride or iodide and methylnormeconic acid, or, rather, methyl-normeconin, $C_9H_8O_4$. By similar means, narcotine can be converted into methylnornarcotine, $C_{20}H_{19}O_7N$.

"These three papers by Foster and Matthiessen made a long step forward in the knowledge of the constitution of the alkaloids, and may, indeed, be termed classical. The accuracy of the work has been amply confirmed by subsequent investigation.

"While this work was in progress, Carey Foster published two papers, entitled 'On Chemical Nomenclature, and chiefly on the Use of the Word *Acid*.' Both appeared in 1865 (*Phil. Mag.*, [iv], **29**, 262; **30**, 57). In these he protests against the word *acid* being used to denote an oxide, and recommends that SO_2 be called sulphurous oxide, SO_3 sulphuric oxide, and $C_4H_6O_3$ acetic oxide.

"In 1869 Carey Foster took part in a discussion on the atomic theory, held at the Chemical Society, the subject having been introduced in a lecture by Professor A. W. Williamson. An account of the discussion will be found in the Chemical Society's *Journal* for 1869.

"Carey Foster's work in chemistry shows that if he had decided to devote himself to that science he would have taken a distinguished position among his colleagues. He was a member of the Council of the Chemical Society from 1865 to 1868, again from 1872 to 1875, and again from 1885 to 1886, and Viice-President from 1888 to 1890. His Fellowship of the Society dates from 1856."

During the early years at University College, Carey Foster made a number of contributions of minor interest to scientific journals, but his first important paper, "On a Modified Form of Wheatstone's Bridge, and Methods of measuring Small Resistances," was read before a meeting of the Society of Telegraph Engineers in 1872 (*Telegraph Engineers' Journal*, 1872—1873, **1**, 196). Previous to this date, Wheatstone's bridge had provided electricians with a convenient and fairly accurate method for comparing resistances, and, as is well known, the result of the experiment expresses the ratio of one resistance to the other. Carey Foster,

however, so modified the bridge method that the difference between instead of the ratio of the resistances was determined. The advantage of the change is only apparent where the resistances to be compared are of nearly equal value, as is generally the case, for instance, in the testing of standard coils; but where this condition is fulfilled, the new method transformed the bridge method from being merely a fairly accurate means of measurement into one of the most refined accuracy, comparable with that attained in the use of a sensitive balance. It also supplied the means of dealing with a very small resistance, such as that of a short, thick wire, by determining the difference between it and the zero resistance of a short copper bar, and it was, indeed, for this alone that the method was first suggested. Carey Foster's method has proved of the highest value to the science of exact electrical measurement, and has made it possible to issue standards of electrical resistance of an accuracy that would otherwise have been impossible of attainment. Alike in its simplicity and its refined accuracy, the method is thoroughly characteristic of his mind. He further showed how the principle involved might be applied to the important process of calibrating the wire of the bridge.

In 1881 Carey Foster published "An Account of Preliminary Experiments for the Determination of the Electromagnetic Unit of Resistance, in Absolute Measure" (*Rep. Brit. Assoc.*, 1881, 426). The accurate determination of this important unit had been undertaken by the British Association in 1863, and the value that had been accepted in this country, as well as widely in other parts of the world, was expressed in the "B.A. unit of resistance," the value of which had been determined by a Committee of the Association consisting of Clerk Maxwell, Fleeming Jenkin, and Balfour Stewart. The classical method of experiment adopted by the Committee consisted in revolving a large, flat, closed coil of insulated copper wire about a vertical diameter in the earth's magnetic field and measuring the consequent deflexion of a magnet suspended at its centre. The deflexion was due to the induced current developed in the coil, and this depended on its resistance as well as on the intensity of the earth's magnetic field. The last, however, affecting the induced current and the deflexion equally, although in opposite senses, disappeared in the final equation that expressed the result of the experiment, leaving a relation between the resistance of the coil, its geometrical form and dimensions, and the speed of its revolution.

During the years that had elapsed since the issue of the B.A. unit, the results of other measurements had led to a growing conviction that it was appreciably too small, and Carey Foster

described an experiment in which, whilst the general principle of the British Association experiment was maintained, it was modified in an important detail. The two ends of the wire composing the coil were unconnected throughout the greater part of its revolution; but for a short interval, the centre of which coincided with the transit of the plane of the coil through the magnetic meridian, they were placed in connexion through sliding contacts with the two ends of a standard resistance coil that formed part of an "auxiliary" circuit in which a steady current was maintained by a thermopile. By the principle, originally applied by Poggendorff in the potentiometer, no current is developed in the coil if the electromotive force developed in it by its rotation in the earth's magnetic field is equal to the fall of potential between the two points in the auxiliary circuit with which it is connected, this being the product of the current supplied by the thermopile and the resistance of the standard coil, and the method of experiment consisted in so regulating the current of the thermopile that the deflexion of a sensitive galvanometer included between the revolving coil and one of its points of connexion with the auxiliary circuit should disappear, whilst at the same time the deflexion of the magnet of a tangent galvanometer included in the auxiliary circuit was recorded. The general principle is simple, and a relation is readily established between the resistance of the standard coil, the deflexion of the magnet of the tangent galvanometer, the geometrical form and dimensions of the revolving coil, and its speed of revolution.

The chief refinement that Carey Foster hoped to effect in this modification of the original experiment consisted in the possibility of the *direct* determination of the resistance of the standard coil. In the original experiment, the resistance determined was that of the revolving coil, and the resistance of the standard could only be obtained by subsequent comparison. To obtain the maximum induced current, it was essential that the revolving coil should be wound with copper wire, and as the resistance of copper with that of all pure metals is seriously affected by changes of temperature, it was necessary that the temperature of the coil should be known with great accuracy during the time that the experiment was in progress, a very delicate matter. In Carey Foster's method, however, the resistance of the standard coil was directly determined while it formed a part of a fixed and independent circuit. The wire composing it might equally well be of copper or of one of the many alloys the resistances of which are scarcely affected by changes of temperature, whilst it was an easy matter to determine its temperature with great accuracy. Further, the new method

reduced the correction for the self-induction of the revolving coil, an important and rather delicate detail in the original experiment, to insignificant proportions, but, at the same time, it unfortunately introduced the necessity of taking its capacity into consideration, a feature that Carey Foster did not probably at first realise.

The apparatus for carrying out the experiment was constructed with great refinement, and was erected at University College, and a series of preliminary experiments were made by Carey Foster with the assistance of Mr. G. W. von Tunzelmann. These experiments showed that the method was capable of yielding consistent results, and there is no doubt that a far higher consistency would be possible if they were repeated in a modern laboratory more completely removed from the disturbing magnetic influences of large masses of iron of continually varying temperature. The results were not, however, sufficiently consistent to satisfy the critical judgment of Carey Foster, and the experiment was abandoned. Whilst they were in progress, Lord Rayleigh and Professor Schuster were engaged in repeating the original experiment, adopting precautions that experience of the intervening years had been shown to be necessary, and in 1882 they published an account of their experiments, and during the next ten years independent evidence supplied by other methods has shown the value they obtained to be a close approximation to the truth.

In 1886 Carey Foster contributed a paper to the Physical Society of London "On a Method of determining Coefficients of Mutual Induction" (*Phil. Mag.*, 1887, [v], **23**, 121—129), the method depending on the comparison between the coefficient of mutual induction of two coils and the capacity of a condenser. On forming or breaking a current in one of two coils, the primary, a discharge of electricity takes place through a neighbouring, secondary, coil, the discharge being determined by the coefficient of mutual induction of the two coils; also, if the coatings of a condenser are connected to two points of the primary circuit, a charge, proportional to the resistance of that part of the circuit that is included between the two points of connexion, enters the condenser, and will be discharged on the cessation of the primary current. To combine these two examples of "ballistic" discharge, Carey Foster succeeded in so connecting the two circuits that, on the break of the primary current, the condenser was discharged through the secondary circuit in the opposite direction to that of the induced discharge, and on varying the charge of the condenser by regulating the resistance between the points of its connexion with the primary circuit, its discharge and that of the induced current neutralised one another.

The disappearance of discharge in the secondary was indicated by a galvanometer, and a simple relation was given between the coefficient of mutual induction of the coils and the capacity of the condenser. The capability of the method had been thoroughly tested at University College by Mr. F. Womack, and it had been shown to be capable of yielding results of a high order of accuracy. Carey Foster's method of determining the coefficient of mutual induction between two circuits has taken its place among the accurate methods of electrical measurement.

In 1876 Carey Foster devised a method, based on the principle of Wheatstone's bridge, of tracing the equipotential curves in a sheet of tinfoil conveying an electric current, and in collaboration with Sir Oliver Lodge he published two papers, "On the Flow of Electricity in a Plane Conducting Surface" (*Proc. Phys. Soc. London*, 1876, **1**, 113, 193), in which this method of experiment was adopted. A further paper by Carey Foster and the present writer, "On the Difference of Potential required to give Sparks in Air," was presented to the Physical Society in 1884 (*Chem. News*, 1884, 114). In the method of experiment adopted in this research, potential differences were measured by a modified form of absolute electrometer that had been designed by Carey Foster and that was found to supply an accurate method for measuring potential differences necessary to produce sparks of from 0·1 to 5 cm. in length.

Among Carey Foster's other publications were further articles on "Heat," "Thermodynamics," "Electricity," and "Magnetism" in later editions of Watts's "Dictionary of Chemistry," and in these he fully maintained his reputation for accuracy, clear judgment, and power of scientific exposition. In later years he published a text-book on electricity in collaboration with Professor A. W. Porter.

Carey Foster became a member of the British Association in 1857, and continued to take an active part in its proceedings until late in life. Besides his direct contributions, to which reference has already been made, he was a member of a number of its committees, the more important of which were those on "Standards of Electrical Resistance," "The Selection and Nomenclature of Dynamical and Electrical Units," "The State of Knowledge of Spectrum Analysis," and "Electrolysis." As President of the Mathematical and Physical Section in 1877, he gave an address on "The Mutual Relation between Mathematics and Physics," in which he dwelt on his favourite theme of the importance of accurate measurement as the foundation of discovery in science. He was Treasurer to the Association from 1888 to 1904. He was one

the founders of the Physical Society of London, the first meeting of which was held in 1873, and of which he was President for two years from 1887. He acted as President of the Society of Telegraph Engineers, now the Institute of Electrical Engineers, in 1880 and in 1881. He was elected to the Fellowship of the Royal Society in 1859, acting as one of its Vice-Presidents from 1891 to 1893, as well as from 1901 to 1903, and he took a keen interest in the work of Kew Observatory Committee of the Society. He received the honorary degrees of LL.D. from Glasgow and D.Sc. from Manchester.

From the first, Carey Foster took a deep interest in the reconstitution of the University of London. Whilst fully recognising its services to education in its earlier days, he was sensible of the grievous anachronism by which the University of the greatest city of the world should continue to be solely engaged in examining and in conferring degrees. He had a high ideal of a university as a body of men and women earnestly engaged in the pursuit and extension of knowledge rather than in preparation for examinations, and he strove without ceasing to bring about the foundation of a university in London that should be worthy of it. He was an active member of the many early committees the aims of which were a constructive policy that should achieve his ideal, and he felt keen disappointment when the conflicting of many interests made it impossible of full attainment in the present university, although it received his full and loyal support. He never ceased, however, to look forward to a time when, by further reconstruction, London should possess a university fully worthy of its position, and he welcomed Lord Haldane's Report as indicating the possibility of a further step in this direction, and possibly its full attainment.

The writer is indebted to Sir T. Gregory Foster, Provost of University College, for a sketch of Carey Foster's work while acting as Principal of the College from 1900 to 1904.

"Dr. G. Carey Foster resigned the Quain Chair of Physics in 1898. It was a time of crisis in university affairs in London, as he reconstitution of the University was pending.

"In view of the impending reconstitution, the Council of University College appointed a special committee to consider the position of the College. On the recommendation of this committee, he office of Principal, later changed to Provost, of the College was nstituted. Dr. Carey Foster was invited to be the first occupant f this office. He held it from 1900 to 1904.

"In his capacity of Principal, he was appointed to represent University College on the Senate of the University under its new

constitution. He threw himself heartily into the new problems that arose, and brought to them all his ripe judgment and experience.

"It soon became evident that the new constitution, under which the University was given a teaching side as well as an examining side, made it desirable that University College, which had been originally founded to be the University of London, should be merged into the reconstituted University. Dr. Carey Foster took an active share in the negotiations that led up to the incorporation of the College in the University. He regarded it as 'a step towards securing unity of aim and interest in all that relates to advanced education and the promotion of original research in London.' He hoped that it was the beginning of a movement that would lead to the concentration and the consolidation of university work in London.

"This view is expressed in the final paragraph of his sketch of the History of University College, which is as follows:

"'The step taken by University College has been followed by King's College, which was incorporated in the University on September 1st, 1909. It may be hoped that similar action will be taken by other analogous bodies, and that in course of time the University of London, perhaps with some modification of its present constitution, may become a centre about which the various bodies in London that are qualified to take part in university work may be united into a single organised system, in which they shall supplement instead of competing with each other, each doing the work for which, by its special circumstances, it may be best fitted.'

"During the four years of his Principalship, great progress was made in various directions in the reorganisation and development of university work in London. The plans for the removal of University College School were matured. The buildings formerly occupied by the School were, as a consequence, set free for university purposes. The accommodation provided at University College for university work was materially increased. There was a rapid growth in the intellectual and social activities of the College, and in these Dr. and Mrs. Carey Foster took a prominent share."

At an early period of his work at University College, Carey Foster recognised the importance of practical work in physics as an essential element in scientific education. The first physical laboratory for students had been opened by Magnus at Heidelberg in 1846, and it was followed in 1863 by the addition of a physical laboratory to the University of Berlin. From 1845, Lord Kelvin

had invited his senior students to work in his laboratory, for a time a disused wine cellar, at Glasgow, and his example was followed by Carey Foster, who thus introduced the teaching of practical physics in this country. At the beginning, this work formed no recognised part of the College curriculum, but regular practical courses in physics were arranged in 1867, the laboratories at that time consisting of two of the College rooms, only one of which was fitted with benches. Later, a third room in the basement, known as the "dungeon"—it was indeed a veritable dungeon—was added, and the privilege of working in it was reserved for the professor and students engaged in research. For some years, the only apparatus available was of the simplest character, but instruments were being constantly designed by Carey Foster himself, whilst the designs were executed by a clever Scotch mechanic, William Grant, who acted as his assistant during the whole time of his professorship, and without whom no reference to the laboratory would be complete. Grant, who was quite a character in his own dour way, became a permanent feature of the Physical Department. His love of the apparatus, so much of which he had constructed, and the agony he experienced in seeing it misused, made him a source of terror to all students other than those few who proved themselves worthy to be entrusted with it; whilst many will remember with humiliation his lofty refusal of the tip that was occasionally offered, either from gratitude or from a desire to acquire merit. He was of the most faithful of servants, and was devoted to Carey Foster, whilst each regarded the other with a simple affection of which both alike were worthy. Sir Oliver Lodge, who was a student in the laboratory in those days, and who later became Assistant Professor of Physics at the College, has rendered a grateful as well as a graceful tribute to the educational value of the work done in the old physical laboratory of University College (Letter to *Nature*, December 3rd, 1908).

In the years that followed, physical laboratories for students were opened at other colleges, and it was inevitable that, as many of these were attached to new institutions in which it had been possible to design the buildings with a view to their subsequent use as laboratories, the simple equipment at University College should have been left behind. Carey Foster, in consequence, continually urged the governing body of the College to undertake the building of a physical laboratory that should be worthy of its traditions, although, no doubt by reason of financial considerations, his representations were for a long time without success. At length, however, he had the satisfaction of preparing the plans for the present laboratories, which were opened to students in

1893, and form a fitting memorial to the value of his work as Professor of Physics. There was an old asphalted tennis court within the College walls from which some of us have often returned in exhilaration, although with begrimed hands and flannels, and now only lives in memory; the building that now occupies its former site is the "Carey Foster" Laboratory.

His nervous manner prevented Carey Foster from ever becoming a good lecturer, and his failure in this respect was perhaps due, in addition, to a conscientiousness that made it difficult for him to be content with a simple statement that he knew to be only an approximate expression of a truth, and at the same time made him reluctant to adopt the customary method of illustrating physical laws by the use of simple, although entirely imaginary, experimental data. In place of these, his illustrations would often consist of the actual results of laboratory measurements, and the younger students, unless they were of a rather exceptional type, were apt to lose both attention and interest in the details of laborious computation. The more able students, however, were inspired by this very quality in their teacher. They grew to reverence exact expression and to regard it as the foundation of all scientific knowledge. They continually brought their difficulties to the Professor, and were encouraged to do so by his unlimited patience in dealing with them. It was not unusual to find Carey Foster surrounded by a small group of students engaged in close discussion half an hour after the close of a lecture, although the dining-room had long since claimed the attention of the rest of the College.

The same quality of enthusiasm for his work and his infinite patience in dealing with its smallest details appeared in his work in the students' laboratory. He never found lecturing easy, but after having given a lecture in the morning and having a further lecture for senior students in prospect at the close of a long afternoon, he would frequently come to the help of some duffer in difficulties in the laboratory, and would devote the best part of an hour to the details of a simple experiment in physical measurement. On these occasions, indeed, there was a danger of his being led by his own love of accurate detail, not only to conduct the whole experiment himself, making all the observations, but to carry out whatever computation might be involved, while the student looked on wonderingly, as from a distance. It may be that some who have worked in the old laboratory at University College in those days have preserved the scraps of paper covered with logarithmic calculations that Carey Foster often left on the

benches, all executed in his wonderfully neat writing, as a memento of the most patient of teachers and most lovable of men, but such prescience is rarely bestowed on youth.

His nervousness made conversation with Carey Foster difficult, even to those who came to know him intimately. Whilst, however, it remained a source of some embarrassment to them, his friends came to regard it as so essentially a part of him that it too became lovable, and they would have felt still more embarrassed if he had suddenly succeeded in overcoming it. Closely associated with his manner was a quaint and entirely original sense of pure humour, that found frequent opportunity for expression both in his professional work and in his private life. That his nervousness and hesitation did not arise from any defect in character would be shown, were any such evidence necessary, from his letters. In these, Carey Foster found no difficulty in expressing himself with perfect clearness and precision, whilst both were emphasised by the beauty and strength of his handwriting. It was in his letters, perhaps, that his quaint humour found its best opportunity for expression. Through the kindness of Mrs. Minchin, the writer has before him a number of letters written by Carey Foster to her husband, the late Professor G. M. Minchin, which are so characteristic that little apology is necessary for the introduction of a few short extracts. A close friendship existed between Carey Foster and Minchin, and in their unassuming simplicity and gentleness there was much resemblance between the characters of the two men. Carey Foster had a profound respect for Minchin's mathematical powers, and consulted him when he felt a doubt as to his own grasp of the mathematical treatment of a physical problem, whilst Minchin had an equally deep regard for Carey Foster as an authority on physical matters, and has expressed his regret to the writer that Foster's nervous manner, together with his extreme modesty, should have made it difficult for some, even of his friends, to realise his true greatness.

The first extract is from a letter dated 1882:

"My dear Minchin,

"The lesson of the day touching electric endosmose is written in the First Book of Wiedemann, beginning at the 392nd verse of the second chapter . . . wherein it is written how the ions do wander when a current passeth through their midst. This, I take it, is the whole secret of electric endosmose; the porous diaphragm causeth not the flow, but maketh the same manifest by hindering the return thereof."

The second is also dated 1882:

"My dear Minchin,

"I hope the enclosed may serve your rivereuce's purpose. Sure, and it's bad I did not write before. But I had to think, and that goes slow.

* * * * * *

"As to your telegraphic friend; let him take to himself a tangent galvanometer and a set of resistance coils, and sundry cells according to Daniell and Grove. . . ."

and then follow instructions as to what the telegraphic friend should achieve.

An extract from a letter referring to a fairly well-known man:

"The gentleman's surface integral suggests to me a considerable amount of self-esteem. But I am willing to believe that the charge is purely superficial. . . . I am told by a friend who knows him much better than I do that he is a good fellow."

And the last is from a letter written in 1887 congratulating Minchin on his marriage:

"My dear G. M. M.,

"I heard awhile ago that you had entered into combination and were no longer a dissociated atom. Accept my warmest congratulations and my fervent hope that you may appreciate the blessings of home rule more fully from year to year."

Several of the letters deal with Minchin's work with photo-electric cells.

The private life of Carey Foster was one of quiet beauty. His transparent honesty and high regard for truth earned him the respect of his friends, whilst has unvarying kindness and courtesy won their affection. In 1868 he married Mary Anne Frances, daughter of Andrew Muir, of Greenock. Recalling that time, Dr. Forster Morley writes:

"It seems only yesterday when my father (the late Professor Henry Morley) said to me, 'I have been walking round the Square with Carey Foster, who has just told me that he is engaged to be married, and has been speaking most charmingly on the subject of love of a man for a woman.'"

There was a striking resemblance between the character of Mrs. Foster and that of her husband, and she even acquired a suspicion of the nervousness that was so strongly marked in him, that, however, only accentuated a natural charm of manner in her. There were born to them four sons and four daughters, all of whom are still living. The mutual confidence that existed between Carey Foster and his wife, and the evident affection with which both parents were regarded by their children, gave a peculiar charm to the visits of the many friends who were always welcome to their home. Mrs. Foster died in 1917, and a year and a-half later Carey Foster's body was laid to its last rest beside hers in the peaceful cemetery at Rickmansworth.

Among the number of Carey Foster's old students at University College who have become distinguished were Prof. W. E. Ayrton, Sir Oliver Lodge, Dr. H. Forster Morley, Prof. Viramu Jones, Prof. A. P. Chattock, Prof. J. A. Fleming, Prof. T. Hudson Beare, Prof. A. W. Porter, Prof. F. Womack, Prof. J. Sakurai, Sir Victor Horsley, and Prof. W. D. Halliburton. It is from his having been first a student, then a demonstrator, and thereafter a friend of Carey Foster that the writer has been able to pay in this notice his last tribute to the memory of one he loved and admired.

A. H. Fison.

WILLIAM JOEL KEMP.

Born 1841; Died March 22nd, 1918.

William Joel Kemp was born at Bow in 1841. He was the youngest of three sons, and was educated at Stock's Academy at Poplar. Owing to his father's death, he left school at a very early age, and was placed in the office of a ship's broker. Finding this work very uncongenial, he induced his relatives to article him to Carters and Green, builders of the famous China tea clippers, in the yard which subsequently became the headquarters of the Thames Ironworks and Shipbuilding Company. His apprenticeship commenced at an unfortunate time, for wood was rapidly being replaced by iron in the construction of ships, and the old-established firms which did not move with the times were being left behind. All the same, this period of his life must have been a particularly happy one. He met all sorts of seafaring men, and in later life he never tired of relating anecdotes connected with their superstitions and adventures, and it is not unlikely that their experiences quickened

the sense of imagination which served him so well in after years. Shortly after completing his articles he married Mary, the daughter of John Cayzer, who organised the emigration to Australia of the East Anglian farm labourers in the starving 'forties and 'fifties. About this time he entered the service of Rickett Smith and Company, coal and coke shippers, as buyer. In this capacity he was brought in contact with the lime burning, plaster, and kindred industries, and when in 1876 a company was formed to work the bed of gypsum discovered four years earlier through the Sub-Wealden boring at Netherfield, Sussex, he took a small financial interest in the undertaking. It was about this time that the necessity for technical education and scientific training was first accepted in England. In 1879 the City and Guilds of London Institute for the Advancement of Technical Education was formed, and almost immediately courses in chemistry under Armstrong in temporary premises in Cowper Street, Finsbury, were advertised. Although nearly forty years of age, Kemp, knowing that the manufacture of plaster at Netherfield rested entirely on rule-of-thumb methods, determined to take advantage of the facilities which the City Guilds Institute afforded and to become an efficient chemist. At Cowper Street he worked for one or two days a week, encouraged and inspired by Armstrong, and he soon proved himself to be not only a logical thinker, but an expert manipulator. The other students in the laboratory were all boys, and the writer, who worked at the bench adjoining Kemp's, shared with them the admiration of his power of application and of his rapidly acquired skill. Kemp, influenced by Armstrong's spirit of research, soon began to make investigations on the production of sulphur from gypsum and from alkali waste, and these occupied him for several years. He was the first to suggest making alkali waste into a paste with water and pumping carbon dioxide into the sludge contained in an inverted conical vessel, thus making the gas do its own stirring and bringing every particle of the waste in contact with it. Some of the results of these investigations were subsequently embodied in Rawes's patents, which were worked by Chance. During these years, the position of the Sub-Wealden Gypsum Company at Netherfield had become very critical, the output had fallen below 40 tons a month, the quality of the plaster was bad, and creditors were clamouring for payment of their accounts, which there were no funds to meet. There was already on the bank an immense tonnage of dump, a grey stone considered useless, which had to be hauled to the surface with the white gypsum, and it was becoming increasingly difficult and expensive to dispose of it on the surface. A meeting was held with the object of winding up the company,

but Kemp, who had already begun to experiment with the grey stone, which consisted almost entirely of gypsum, persisted in the view that under proper direction the operations of the company would be successful. Two of the shareholders present were impressed, and agreed to provide further funds if Kemp would undertake the management, and it was thereupon decided that operations should be continued. Kemp's experiments with the grey stone were now pushed on, with the result that in a short time he had perfected a method whereby the waste was converted into a plaster of the Keen's cement variety, which, although dark in colour, set hard and evenly. He introduced this plaster under the name of "Sirapite," and from that day the success of the undertaking was assured. In 1891, 10 tons of "Sirapite" were sold; ten years later the annual sale was 15,108 tons, and in 1911 the sales exceeded 31,000 tons. Kemp's genius was shown not only in the way he attacked his problems on the chemical side, but also in his engineering ability and in the handling of men. From the first he recognised the inefficiency of boilers fed with water almost saturated with calcium sulphate, and within two years of taking control he had scrapped the steam plant and had substituted gas producers and large gas engines. He introduced kilns of large size, which reduced the consumption of fuel and greatly simplified the grinding and mixing plant. He subsequently opened up a new shaft in the mine, which he equipped with electric lighting and haulage plant. Having placed the business on a profit-earning basis, Kemp devoted his attention to the amelioration of the condition of his workpeople. Although himself prepared to work twelve hours a day or more, he reduced in 1895 the working hours to eight and afforded all workmen suitable opportunities for recreation. At his suggestion, the company built a large number of model houses standing in large gardens, which the workpeople were permitted to purchase at cost price. In 1903 Kemp completed his plans by bringing about an amalgamation of the chief makers of plaster in the United Kingdom.

Very few of those who travel by the South-Eastern Railway from Tunbridge Wells to Hastings realise that near Mountfield, hidden from, but within a few hundred yards of, the line, and in one of the most beautiful of the Sussex valleys, lie a mine fully equipped and busy works employing several hundred hands, at which a large part of the plaster used in this country is produced. It was here that Kemp conducted his experiments which revolutionised the industry, and it was here, at the scene of his life's work, that he breathed his last. Shortly after the outbreak of war his son, who for some years had assumed the management, volunteered for

service, and Kemp, then seventy-five years of age, returned to take charge. Always confident and cheerful, ever hard-working, he resumed his former duties with an activity and interest which might have been expected from a man thirty years his junior. On the morning of March 22nd, 1918, he rose in the usual health and spirits, but shortly afterwards, when about to go the round of the works, he suddenly expired.

GERALD T. MOODY.

SYDNEY LUPTON.

BORN JANUARY 3RD, 1850; DIED JULY 10TH, 1918.

SYDNEY LUPTON, who was elected into the Society in 1872 and remained a Fellow until his death, was the youngest and last surviving son of Darnton Lupton and of his second wife, Anna Jane Busk. He was born at Eller Close, Roundhay, near Leeds, on January 3rd, 1850. His father, a member of a well-known Yorkshire family, was head of the firm of William Lupton and Co., woollen manufacturers. He was a man of considerable influence and public spirit, much respected, and took a leading part in the municipal politics and social life of the town and district.

His son, the subject of this notice, was educated at Rugby and lived in Dr. Jex Blake's house. From Rugby he passed to Oxford, where at Christ Church he came under the influence of Dr. Vernon Harcourt, and was led to devote himself to science, particularly to mathematics and chemistry.

On leaving the University, after taking his degree, he was appointed a science master at Harrow School. The work of school teaching was not uncongenial to him, and he had a fair measure of success in it; but his mother—now a widow—having fallen into indifferent health, he resigned his position in order to live with her at Harehills, near Leeds, where he established a small laboratory and continued to occupy himself with experimental work.

It was during this period that the writer of this notice made his acquaintance, and had the opportunity of observing the progress of his inquiry on the slow oxidation of potassium, the longest and perhaps the most important of his investigations. On the death of Mrs. Lupton he took a smaller house at Roundhay, where he continued to live until his removal to London in 1896.

During his residence in Leeds, Lupton took part in the civic life of the town, was a member of the Board of Guardians, and

was associated with the late Canon Jackson, Vicar of St. James's, in many charitable objects. For four years he was a member of the Committee of Management of the Cookridge Convalescent Hospital, and on his resignation, consequent on his leaving Leeds, his fellow-members recorded their appreciation of his genial and energetic help and their sincere thanks for his services "during a period requiring special administration." This last sentence has reference to the assistance he was able to render the institution in connexion with the erection of a wing to the building to perpetuate the memory of his friend, Canon Jackson.

Lupton's intellectual tastes led him to take an interest in the activities of the Leeds Philosophical and Literary Society, where he occasionally lectured on scientific subjects. He became a member of its Council in 1885–6, Honorary Secretary from 1886–95, and a Vice-President in 1895–6.

Practically the whole of Lupton's experimental work was done during his residence at Leeds. His first published paper, "On the Formula of the Alums," appears in the *Journal* of the Society for 1875. Although the doctrine of valency, which we owe to Frankland, was fairly well established at this period, there was considerable uncertainty as to the true formulæ of a number of inorganic compounds, owing to doubt as to the valency of particular elements. This was the case with the group of the alums. Lupton, at the suggestion of Dr. Vernon Harcourt, sought to establish the generic formulæ of these salts, independently of considerations of the combining values of their constituents, by a study of the conditions under which they lose their water on heating or on exposure to a dehydrating agent under reduced pressure, and he showed conclusively that they must contain at least twenty-four molecules of water, whence the general formula now universally accepted follows.

In the same year he published a note on the preparation of cuprous chloride, in which he described the different mode in which water acts on this substance, depending on its method of formation (*Chem. News*, 1875, **30**, 233). This was followed in 1876 by a number of short notices (*Chem. News*, 1876, **33**, 90). He showed that in preparing nitrogen by the well-known method of passing air over red-hot copper turnings, the operation might be rendered continuous by mixing the air with ammonia gas, whereby the cupric oxide was reduced as fast as it was formed, or, as is more probable, by the metal acting catalytically and inducing the production of water:

$$3(2N_2 + O) + 2NH_3 = 3H_2O + 7N_2.$$

In this manner, only a relatively short length of heated copper turnings is needed, and the action proceeds uninterruptedly.

In another communication, on the "Solubility of Naphthalene in Water," he sought to disprove Garden's contention that Plateau's theory of the cause of the movement of this substance on the surface of water was invalid by showing that its solubility, and consequent high tension of its solution, are sufficient to account for the phenomenon.

He further described a number of reactions serving to distinguish aniline from naphthylamine, and made known a number of characteristic tests for succinic acid.

Lupton's most important chemical paper was his study of the "Slow Oxidation of Potassium," communicated to the Society in 1876 and published in the *Journal* for that year, in which he carefully repeated the observations of Davy, Berzelius, Gay Lussac and Thénard, and Harcourt, and sought to clear up certain discrepant statements with regard to the number of potassium oxides capable of existence. He confirmed Vernon Harcourt's work, made fourteen years previously (*Quart. Journ. Chem. Soc.*, 1862, **14**, 267), carefully watching the colour changes which follow the progress of the oxidation, and analysing the products at the several stages by a method he devised, and of which he proved the sufficiency. He was disposed to regard the existence of the grey suboxide, K_4O, of Berzelius as improbable, and he concluded that the intermediate products of oxidation were mixtures of K_2O and K_2O_2 in variable proportion, depending on temperature and time and the nature of the oxidising medium. He compared these intermediate products with the successive stages in the oxidation of lead and with the several lead oxides described by various observers, the general nature of the change being similar. He obtained analytical numbers for the yellowish-green product which corresponded with the composition of a dioxide, K_2O_2, and described a number of reactions which appeared to indicate its individuality. He gained no certain proof of the existence of the trioxide, K_2O_3, but was inclined to regard the brownish-yellow stage of the colour change as some evidence of its formation. He states that "the more thoroughly the air is dried, the less is its oxidising action," as proved by Baker (*Phil. Trans.*, 1888), and subsequently by Holt and Sims (T., 1894, **65**, 434), who showed that potassium may be distilled unaltered in perfectly dry oxygen.

Lupton's conclusions have been confirmed, in the main, by the last-named observers, although they found it impossible to associate the differences of colour with oxides of definite composition, the oxidation proceeding apparently without any break until the

heated mass consisted wholly of the bright orange-yellow peroxide, K_2O_4, described by Harcourt.

Holt and Sims also repeated Lupton's experiments on the action of the oxides of nitrogen on heated potassium, and with nitrous oxide obtained evidence of the formation of the buff-coloured trioxide and the sulphur-yellow dioxide, the existence of which in solution had already been established by Harcourt.

Lupton, in 1888, published a short communication in the *Proceedings* of the Society on compounds of chromium, and in 1891 he contributed to the *Philosophical Magazine* a controversial paper on "The Reduction of the Results of Experiments, with Special Reference to the Hydrate Theory of Solution" (*Phil. Mag.*, [v], **31**, 418), which produced a rejoinder from Mr. Spencer Pickering.

Sydney Lupton was a painstaking and conscientious worker, scrupulously accurate, and a good manipulator, cautious in drawing conclusions or in forming opinions, but very tenacious in holding them when convinced of their soundness. His knowledge and, as his published work shows, his sympathies were almost exclusively confined to inorganic and physical chemistry; and owing probably to the limitations of his early training and his subsequent lack of opportunity, he never seemed to be attracted by the problems of modern organic chemistry.

As a fellow-townsman and a member of the well-known Mill Hill Chapel, he was a great admirer of Joseph Priestley, who formerly ministered in Leeds, and began his chemical career there. At one time he conceived the idea of writing the life of the old philosopher and of bringing out an annotated edition of his complete works, for which he had gradually accumulated material. But to do justice to Priestley's astonishing versatility and the extraordinary range of his knowledge requires an equally exceptional man, and Lupton, after playing with the project for some time, finally relinquished it, being deterred from the attempt in all probability by its very magnitude. He was, however, well qualified to make it, especially as regards Priestley's scientific work and philosophical opinions, for he had considerable critical acumen and literary skill, was an omnivorous reader, and had extensive knowledge of the literature and science of the latter half of the eighteenth century.

On his removal to London, Lupton ceased to take any active part in experimental inquiry. He kept up his interest, however, in scientific work, was a frequent attendant at meetings of scientific societies, and at the lectures of the Royal Institution. He also interested himself in Bedford College, and in the work of St.

George's Hospital, and was for a time a member of its Committee of Management.

He was, perhaps, most generally known by his books on "Elementary Chemical Arithmetic" and "Numerical Tables and Constants in Elementary Science," published by Macmillan's, and based probably on his experience in science teaching at Harrow. His last production was a little book of some 120 small 8vo pages bearing the modest title, "Notes on Observations, being an Outline of the Methods used for determining the Meaning and Value of Quantitative Observations and Experiments in Physics and Chemistry, and for reducing the Results obtained." Notwithstanding the somewhat archaic ring of its title, it is an admirable piece of work, and well worthy of careful study by all engaged in quantitative work. In spite of its diminutive size, it must have involved a wide range of reading, no small exercise of criticism, and considerable skill and thought in arrangement and condensation. It shows Lupton at his best. It is a model of clear, restrained statement and rigorous logic, and should find a place in every physical and chemical laboratory.

At all periods of his life, Lupton was fond of travel, and his ample means made it easy for him to make extensive journeys. He was an acute observer and a shrewd judge of character, with a keen sense of humour—qualities which, added to his wide reading and knowledge of history and his readiness to communicate his knowledge, made him interesting as a companion.

He died at his London house, 102, Park Street, Grosvenor Square, on July 10th, 1918, and was buried at St. John's Cemetery, Roundhay. He showed his interest in the work of the Chemical Society by bequeathing to it his valuable chemical library.

T. E. Thorpe.

GEORGE MARTINEAU, C.B.

Born 1835; Died February 5th, 1919.

By the death of Mr. George Martineau, which occurred after a brief illness at his residence, Gomshall Lodge, Gomshall, Surrey, we have lost a member of an old and distinguished family and a man who was perhaps the greatest authority of his time in this country on sugar from its economic point of view. The deceased was the son of Mr. George Martineau, of Tulse Hill, and grandson of Mr. David Martineau, who in 1797 established the sugar refining firm which, as David Martineau and Sons, was at one time the largest in London; it has remained in the family for more than a

century. The fact is not without interest to our Fellows that this firm was one of the first, probably the first, in this country to recognise the value of scientific control, and the partners appointed the late Mr. C. Haughton Gill, F.C.S., first as their chemist and subsequently as their manager.

Mr. Martineau was educated at University College, London, and on coming of age entered his father's business, in which he was actively associated until his retirement in 1896. His connexion with sugar refining was on the commercial side, but he always took a keen interest in the general technology of the industry. Although a Liberal of the Gladstonian school, he recognised the defects of our fiscal system more than forty years ago; and in 1872, when the effects of the foreign sugar bounties began to make themselves felt, the British refiners appointed a Committee with Mr. Martineau as Secretary. This Committee visited the principal beet-growing countries of Europe. Thus commenced the anti-bounty campaign, which culminated in the abolition of the bounties by the International Convention of 1902. In recognition of his services, Mr. Martineau was appointed a Companion of the Bath by King Edward VII.

Imbued with the true scientific spirit, Mr. Martineau possessed a thoroughly logical mind, clearly shown by his numerous writings, which were continued up to the last days of his life: it may be said, indeed, that he died in harness. He was a chemist by instinct, and few commercial men had a greater appreciation of chemistry and chemical research. Keeping himself *au courant* with all the chief events in the progress of our branch of science, it was doubtless with this object that he became a Fellow of the Chemical Society in 1871. It cannot be forgotten that, equally with those members of his firm connected with the practical side of sugar refining, he shared a strong belief in the precise methods which chemical analysis affords when applied to commercial questions. In this connexion, we may point out that he was a pioneer in the establishment of the Beetroot Sugar Association of London, the functions of which were to check the weights and make analyses of the whole of the raw beetroot sugar shipped from the Continent to the Port of London.

Mr. Martineau's memory will be cherished by many. His charming personality, gifted conversational powers, wide erudition, and his deep sincerity had secured for him a wide circle of friends. Not a few have reason to be grateful to him for the assistance and encouragement he gave them at the commencement of their careers; but from these he resented open thanks, being quite content to view their progress with silent satisfaction.

ARTHUR R. LING.

SIR ALEXANDER PEDLER, F.R.S.

BORN MAY 21ST, 1849; DIED MAY 13TH, 1918.

LIKE many other chemists who have attained an eminent position in the scientific world, Pedler began life in connexion with pharmacy. His father, Mr. George Stanbury Pedler, was in business as a pharmacist at 199, Fleet Street until, on the removal of old Temple Bar and the widening of Fleet Street, preparatory to the erection of the Law Courts, the premises were swept away.

Pedler received his early education in the City of London School, which he left at midsummer, 1865. In October of the following year, at the age of seventeen, he won a Bell Scholarship, and began work as a student in the laboratory of the Pharmaceutical Society in Bloomsbury Square. Here he went through the usual course of analytical work, and at the end of the session he was awarded a certificate of honour in practical chemistry. Before leaving, he began a piece of research suggested to him by the present writer, who was at that time Demonstrator in the laboratory. It was with great regret that he parted with the promising young student, who by this time had decided to leave the comparatively narrow field of pharmacy and proceeded to place himself under Professor (afterwards Sir Edward) Frankland, at the Royal College of Chemistry, then in Oxford Street. There, after carrying on his studies for two years further, he assisted Frankland in the separation of the amyl alcohols of fousel oil by Pasteur's process. This work was done in the laboratory of the Royal Institution, where Frankland had held the Professorship of Chemistry in succession to Faraday since 1863. From the optically active and inactive alcohols, Pedler prepared the corresponding valeric acids, and gave an account of his work to the Chemical Society in 1868 (*Journ. Chem. Soc.*, **21**, 74). Further work in this direction was interrupted by his taking part in the solar eclipse expedition to Sicily in that year.

From 1871 Pedler served for two years as lecture demonstrator to Sir Edward Frankland in the Royal College of Chemistry in succession to Mr. Herbert McLeod, who had been appointed to the professorship of chemistry in the then newly instituted Royal Engineering College at Cooper's Hill. At the same time, he assisted in the research work on gaseous spectra in which Frankland and Lockyer were jointly occupied. This naturally directed Pedler's attention to the fascinating problems connected with the physical constitution of the sun and the stars. Consequently, on receiving

in 1873 appointment as professor of chemistry in the Presidency College, Calcutta, he naturally occupied himself with subjects connected with celestial chemistry, and soon after his arrival in India he was charged with special duty in connexion with the eclipse expedition of 1875.

On joining the Presidency College, he found that no practical work in any department of science was done by the students. To remedy this deficiency in the scheme of instruction was his first care, and ultimately he succeeded in securing the introduction of a small amount of practical work into the science course for the M.A. degree, and a practical examination was held for the first time in 1882. Ultimately, he had the satisfaction of finding the university regulations require every college sending up students to provide the necessary staff and appliances for teaching practically each of the departments of science, and each candidate for B.A. or B.Sc. degree to be examined practically.

Having been born in 1849, Pedler was still a very young man on reaching India, and those who knew him in his early days will gladly recall those features of his character which made him not only popular in youth, but, remaining unchanged to his latest years, contributed materially to his success in official life.

In India Pedler retained the professorship in Calcutta, together with the office of Meteorological Reporter to the Government of Bengal, for twenty-two years. He then became Principal of the Presidency College and Vice-Chancellor of the University. In 1899 he was appointed Minister of Public Instruction in Bengal, and became an additional Member of the Legislative Council under the Viceroy.

Among other institutions, Pedler took great interest in the Ravenshaw College at Cuttack, and was instrumental in obtaining accommodation for the physical and chemical departments in that institution. These successive steps in official life explain the fact that Pedler's original contributions to scientific chemical literature were limited to the one paper on valeric acids, already mentioned, and several which arose out of the circumstances of his residence in India.

Soon after his arrival in that country, he examined and reported on the coal-gas and water supplies of Calcutta. In 1878 he sent home a paper on the poison of the cobra, which was printed in the *Proceedings* of the Royal Society (**27**, 17).

In 1890 he contributed to the *Journal* of the Chemical Society three papers, which showed that he was utilising opportunities, previously neglected by chemists, of studying the action of tropical sunlight on chemical change. The first of these papers was entitled

"The Action of Light on Phosphorus and some of the Properties of Amorphous Phosphorus." The second paper was on "The Action of Chlorine on Water in the Light, and the Action of Light on certain Chlorine Acids." The third paper contained an account of attempts to estimate hydrogen sulphide and carbon bisulphide in gaseous mixtures by explosion with oxygen.

Pedler was a Fellow of the Institute of Chemistry and of the Chemical Society. He was elected F.R.S. in 1892. He was also an honorary member of the Pharmaceutical Society.

In recognition of his public services in India he was created C.I.E. in 1901, and on his return to England in 1906 he received the honour of knighthood. On his retirement he soon found occupation in public work; he became honorary secretary to the British Science Guild, which owes much to his devoted service, and on the outbreak of war he took up active duties connected with the research department of the Ministry of Munitions. Whilst attending a meeting of Committee at that office on Monday, May 13th, 1918, he was seized with sudden illness and expired immediately. His death came as a great shock and surprise to his many friends, among whom no suspicion of weakness had been entertained.

Pedler was twice married, first in 1878 to Elizabeth Margaret, daughter of C. K. Schmidt, of Frankfurt, and, secondly, to Mabel, youngest daughter of the late Mr. W. Warburton, R.N., of Dedham, who survives him. He left no children. W. A. T.

JOSEPH PRICE REMINGTON.

BORN MARCH 26TH, 1847; DIED JANUARY 1ST, 1918.

JOSEPH PRICE REMINGTON was born at Philadelphia on March 26th, 1847, and belonged to a well-known Quaker family, his ancestors having been for three generations members of the Society of Friends. His father, Dr. Isaac Remington, was a prominent Philadelphia physician, whilst his mother, the daughter of John Hart, was in a direct line of descent from an apothecary who practised his art in Philadelphia early in the eighteenth century. An inclination for the professional pursuit of pharmacy, which was manifested by Remington at an early age, would thus seem to have been inherited.

At the comparatively early age of fifteen years, Remington

suffered the loss by death of his father, and this appears to have affected his subsequent career; for a plan to supplement his preliminary education—obtained in private schools and in the high school at Philadelphia—by an academic course of study had to be abandoned. In 1863 he entered the establishment of Charles Ellis, Son and Co., a firm of wholesale druggists in Philadelphia, where he remained for four years, and during that time he attended evening lectures at the Philadelphia College of Pharmacy, from which he graduated in 1866. During the years from 1867 to 1870 Remington was employed in the manufacturing laboratories of Dr. E. R. Squibb, at Brooklyn, N.Y., and in this position he had exceptional opportunities for acquiring a knowledge of technical methods, especially in their application to chemical and pharmaceutical products, whilst also enjoying intimate association with a man who was widely known for his scientific attainments and exceedingly high ethical standards. Remington then returned to Philadelphia, and after a short period of service with the firm of Powers and Weightman, manufacturing chemists of that city, he established a pharmaceutical business on his own account, which was successfully conducted for thirteen years. In the meantime, he had also served as an assistant to Professor Parrish, and subsequently to Professor Procter, at the Philadelphia College of Pharmacy, and on the decease of the latter, in 1874, he was elected to the professorship of pharmacy in the college which had been his *alma mater*. The position which Mr. Remington was thus called on to fill he retained for the exceptionally long period of forty-four years, or until the close of his life, and during that time several thousand students had received instruction from him.

As circumstances did not permit Professor Remington to acquire a scientific training, in the modern sense, his attainments and talents were directed more to what may be termed the practical side of pharmacy and to editorial work. As examples of this activity, there may specially be noted his participation in several revisions of the "United States Dispensatory," the publication of his well-known text-book, entitled the "Practice of Pharmacy," and the arduous duties committed to him as Chairman of the Committee of Revision of the "United States Pharmacopœia."

Professor Remington was a Fellow of the Chemical, Linnean, and Royal Microscopical Societies of London, as well as an active member of several scientific societies in his own land. The esteem in which he was held by his professional colleagues had, moreover, been manifested by the bestowal of honorary membership in a large number of pharmaceutical organisations both at home and abroad. He had travelled widely in his own country, and had

several times visited Europe, the last occasion having been in the autumn of 1913, which will still be pleasantly remembered by many of his English friends.

The home life of Professor Remington, with a devoted wife and several children, was particularly happy. His genial nature and fluency as a speaker, together with the fund of interesting information which he possessed, rendered him a most pleasant companion. In social as well as professional circles he was therefore always gladly seen, and accorded a prominent place.

The writer of these lines is grateful for the privilege of rendering a slight tribute to the memory of one with whom a friendship had been sustained for more than forty years, and whose qualities of mind and heart had won such extended appreciation and regard.

F. B. Power.

JEAN JACQUES THÉOPHILE SCHLOESING.

Born July 9th, 1824; Died February 8th, 1919.

One of the oldest and most distinguised of the foreign members of the Society, Jean Jacques Théophile Schloesing, passed away on February 8th of this year. He was in his ninety-fifth year, and almost all his life had been associated with agricultural chemistry. He knew its illustrious founders, Boussingault, Lawes, and Gilbert, when they were still young men almost at the beginning of their careers; he introduced new ideas at a critical stage, and, finally, when development had temporarily ceased, he opened up a new path, which is still leading to fruitful results.

Schloesing was born at Marseilles on July 9th, 1824. At the age of seventeen he entered the Polytechnic School, and left it two years later to take a post in the "Service des Manufacteurs d'Etat." He thus began his career at the most eventful period in the history of agricultural chemistry; it was the year, 1843, in which Lawes and Gilbert started their great work at Rothamsted, one year after Liebig's famous report on agricultural chemistry to the British Association, and four years after Boussingault had commenced his striking investigations at Bechelbronn.

He must have done well in his first post, for three years afterwards—in 1846—he became Director of the École des Tabacs, and within a few months published his first paper in the *Comptes rendus*; it was on nicotine and its estimation in leaf and manu-

factured tobacco. He was the first to obtain nicotine in any quantity; it had previously been prepared, as he tells us, only in "quelques rares échantillons." Schloesing verified its composition and designed a method for estimating it within about 1 per cent.—a very accurate determination for the time. The method consisted in displacing the nicotine with ammonia, extracting with ether, eliminating the excess of ammonia by the evaporation of the ether, and then titrating the residual base with sulphuric acid. For five years no further publications appeared, then followed an ingenious paper on the determination of ammonia in tobacco; milk of lime was added, and the mixture placed over sulphuric acid in the cold. The ammonia volatilised, and was absorbed by the acid, but at the low temperature of the experiment no decomposition of other substances occurred. This paper was followed shortly afterwards by one on the estimation of nitrates in presence of organic matter; hydrochloric acid and a ferrous salt were added, and nitric oxide produced; this was washed free from hydrochloric acid, then mixed with air or oxygen, converted into nitric acid, and titrated with an alkali. Subsequently, however, Schloesing found that conversion into nitric acid was unnecessary, and he designed a method for direct measurement of the nitric oxide. He also introduced considerable improvements into the methods for estimating ammonia in dilute liquids, such as rain. As an illustration of the very cumbersome nature of some of the methods then in vogue, it may be mentioned that the determination of ammonia in rain-water at Rothamsted, carried out in 1853, had involved the distillation of 2 cwt. of rain and evaporation of the distillate with sulphuric acid; in spite of all the laborious care bestowed on the work, the figure obtained was probably double the true value.

For the next seven years Schloesing published no scientific work, but from 1860 onwards he issued a number of important publications. In 1860, also, he began some cultural experiments with tobacco, which lasted for fifteen years, and were designed to ascertain whether the physical properties and nicotine content of the leaf are characteristic of the variety or the result of environmental factors. In the first series, tobacco was raised from samples of seed coming from various regions; the resulting leaf had in each case the physical characters and nicotine content characteristic of the parent plants grown in their original home. The second series was more extended and lasted fourteen years; its purpose was to discover whether any marked alteration occurred in the characteristic properties when a variety is cultivated in a new district. Havanna tobacco was grown, and the seed saved; some was sown and some was stored; each year a certain quantity of the seed of

each generation was sown. In no case was any difference observed.

In 1866 Schloesing began his investigations on the soil. It was probably in this subject more than in any other that the genius of the man shone out. Looking back at these papers, their striking feature is their modernness; one can well believe that at the time of publication they would not be fully appreciated. Again and again he broached new subjects, which neither he nor his contemporaries developed, but which later workers rediscovered thirty or forty years afterwards and showed to be of signal importance. He was essentially a pioneer rather than a builder, and he had the extraordinarily good fortune to discover gold almost every time; but he never himself developed his "finds," and the subject was not sufficiently well organised to ensure that others should develop them for him.

Schloesing's period of greatest activity was from 1866 to 1879, when he was between forty-two and fifty-five years of age; during this time he opened up no fewer than five new fields of soil investigation, three of which are now proving extremely valuable. His first soil paper was on the soil solution, which he separated from the solid particles by a displacement method. The subject received very little attention for nearly forty years; its importance was not fully realised until Whitney and Cameron in America published their striking paper in 1903, when investigations began again, using at first methods similar to those that Schloesing had designed. At the present time it receives perhaps more attention than any branch of soil chemistry.

Another subject which has come into prominence in recent times was investigated by him in 1868. He showed that nitrates are decomposed during certain fermentations, and five years later he further showed that they are reducible to gaseous nitrogen in soils deprived of oxygen. He also demonstrated that oxidations rather than reductions are the normal phenomena in soils under natural conditions; surface soils readily absorb oxygen, whilst sub-soils do not. After a lapse of nearly thirty years this phenomenon was independently rediscovered, and its investigation figures prominently in some of the most recent research programmes.

His most important work, however, was on nitrification. For a long time it had been known that nitrates are gradually formed when plant or animal residues, farmyard manure, etc., are incorporated in the soil. The process was of much technical importance in the seventeenth and eighteenth centuries as the source of nitrates for gunpowder. During the Thirty Years' War and other great continental wars, the various governments had been seriously

concerned in these so-called nitre beds, and had done a great deal to stimulate their development. An interesting collection of memoirs relating to the practical details was published in Paris in 1776.* A study of these papers shows that the conditions of the change were tolerably well ascertained even then, but nothing was known of its mechanism.

It has several times happened in the history of civilisation that agriculture has benefited by knowledge gained during war. The mass of information accumulated during the eighteenth century wars, and apparently rendered useless in the nineteenth century by the promise of peace and the discovery of nitrates in Chile, was found to be of fundamental importance in agriculture. Boussingault had realised, and Schloesing at once accepted the view, that the nutrition of plants, so far as nitrogen was concerned, depended on the nitre-bed processes; organic nitrogen compounds, useless as plant nutrients, became converted into highly valuable nitrates when added to the soil; the more rapidly this change could be brought about, the better for the plant. So long, however, as the mechanism of the change was unknown, the old knowledge was simply empirical and incapable of full utilisation. Many investigations had been made, but the problem remained unsolved. The balance of opinion was in favour of a purely physical process, but there was also a strongly supported chemical hypothesis.

In 1875 a Commission was appointed to inquire into a scheme for carrying Paris sewage out to the land between Clichy and the forest of St. Germain, and Schloesing was asked to draw up the report. Rarely, even in France, can an essentially practical inquiry have led to such striking scientific results. When Schloesing had finished the investigation, he had not only discovered a new and vastly improved method of treating sewage, but he had realised what was the cause of nitrification, and thus founded the science of soil bacteriology. We cannot do better than let him tell the story in his own words:

"I was selected," he tells us, "to draw up the report of this Commission. On this occasion, following the plan indicated in 1856 by M. Hervé Mangon, and taking advantage also of the more recent investigations of Dr. Frankland, I endeavoured to elucidate the principles involved in the land treatment of sewage by connecting the process with the phenomena of slow combustion of organic matter in an atmosphere containing oxygen; I investigated at the same time the conditions necessary to secure satisfactory

* "Receuil de Mémoires et d'Observations sur la formation et sur la fabrication du Salpètre par les Commissionnaires nommés par l'Académie pour le jugement du Prix du Salpètre."—Paris, 1776.

purification in practice. I made a special point of distinguishing two problems which were often confused: purification simply and solely of Paris sewage, which would only require an area of 2000 hectares (5000 acres), and agricultural utilisation of Paris sewage, which would require an area twenty times as great.

"Boussingault had just published the researches on nitrification that he had carried out some time previously. Blood, meat, wool, straw, and oil-cake did not nitrify when mixed with sand and chalk and allowed slowly to oxidise, but they rapidly nitrified when mixed with soil. I had vainly tried to nitrify ammonia by adding it to sand and chalk and leaving the mixture exposed to air. These results led me to think that the property of bringing about nitrification was peculiar to soil.

"Wishing to fix my ideas on the subject, I made the following experiment. A large tube, 1 metre long, was filled with 5 kg. of ignited sand mixed with 100 grams of powdered chalk. The sand was watered daily with sewage, the amount being so arranged that it took eight days to traverse the tube. For the first twenty days there was no sign of nitrification, then nitrates began to appear, and the amount rapidly increased; finally, the liquid flowing out of the tube contained neither ammonia nor organic matter—the sewage was absolutely purified."

The quality of the man's genius was revealed in two striking deductions drawn from this simple experiment. One was of supreme practical importance, and has revolutionised sewage disposal practice.

"Au point de vue de l'épuration des eaux d'égout, l'expérience . . . prouve, en effet, qu'il n'est nullement nécéssaire que l'irrigation soit établie sur les terrains agricoles; de sables steriles se prêtent parfaitement à l'épuration, lorsque le ferment nitrique, apporté par les eaux mêmes, a pris possession du milieu."

From this to the modern bacteria bed is no great step, at any rate in principle.

The second deduction was of even greater consequence for the development of agricultural science. Reverting to the delay of twenty days in the setting in of nitrification, Schloesing and Muntz asked why it set in. With characteristic shrewdness they observed that this delay could scarcely arise if the process were purely physical or chemical; some biological factor seemed to be indicated. In order to test this possibility they added a little chloroform to the sewage; nitrification at once stopped. They then removed the chloroform and "seeded" with a little fresh sewage; after an interval nitrification began again. This showed that the process was brought about by living organisms, and forthwith Schloesing

and Muntz announced the existence of a living ferment. The discovery at once attracted attention; Warington at Rothamsted immediately recognised its importance, and proceeded to investigate nitrification in the Rothamsted soils; he was able to confirm the accuracy of Schloesing's deductions. Later on, the proof was made more rigid by Winogradsky's discovery of the organism. It is no diminution of the credit of the discovery that Pasteur in 1862 had already foreshadowed it, as Schloesing himself pointed out, in his remarkable statement:

"Beaucoup d'êtres inférieurs ont la propriété de transporter l'oxygène de l'air, en quantité considérable, sur les matières organiques complexes: c'est un des moyens donc se sert la nature pour transformer en eau, acide carbonique, oxyde de carbon, azote, acide nitrique, ammoniaque, les éléments des substances organiques élaborées sur l'influence de la vie."

This research marks the beginning of soil bacteriology. It seized the imagination of the younger workers, and speedily attracted recruits to the new subject. Although Schloesing did not himself develop the subject, he was satisfied that the "ferment nitrique" did not exhaust the list of soil organisms. Reverting to his earlier work on the absorption of oxygen by soils, he says in one of his lectures*: "C'était là, pensait-on alors, un fait purement chimique. On sait aujourd'hui que c'est principalement un fait biologique, c'est-à-dire que la combustion observée est le résultat de la vie de nombreux organismes, tel par example que le ferment nitrique, lequel est chargé de transporter l'oxygène sur l'azote."

These investigations by no means represent the whole of his work on soil, although they may well prove to be his most permanent contributions to science.

By a lengthy washing process, he obtained a preparation of the finest clay particles which remained indefinitely suspended in pure water, but was precipitated by traces of a calcium or magnesium salt. This was commonly regarded as being in some sense the essential clay, and agricultural chemists marvelled at the minute amount present even in heavy soils. The conception served a useful purpose, but it has since been replaced by a broader one: the soil is now considered to be made up of particles varying from 1 mm. downwards to molecular dimensions, the different groups merging one into another without perceptible breaks. The clay group is assigned for convenience an upper limit of 0·002 mm., but this is regarded as purely conventional.

Another important investigation had to do with the movements of calcium carbonate in the soil. The conditions of solubility of

* "Leçons de chimie agricole," 1883.

calcium carbonate in carbonic acid were determined, and the relationship between the quantities of these two substances was shown to follow a logarithmic law. Deductions were drawn which threw important light on the practice of liming and marling, and on the presence of lime in natural waters.

During the course of these investigations, Schloesing was appointed in 1876 to the Chair of Agricultural Chemistry in the Institut Agronomique, then just founded. Eleven years later, in 1887, he followed the illustrious Boussingault at the Conservatoire des Arts et Metières. *During his active period, his lectures were* collected by his son in a volume, which still remains a source of inspiration to the student.

In 1875 he began another important group of investigations: he carried out a series of determinations of the amount of ammonia in the air, and published some interesting speculations as to its source. He supposed that a great natural circulation took place: the nitrates washed out from the soil find their way to streams and rivers, and finally to the sea; there they are reduced to ammonia, some of which escapes into the atmosphere, is blown over the land, and there absorbed by the soil or washed down by the rain. The ammonia then nitrifies, and such of the resulting nitrate as is washed out from the soil by rain-water passes once more through the same cycle.

In like manner, he supposed a circulation of carbon dioxide between oceans and atmosphere, and in this way he explained the smallness of the variations in amount of the carbon dioxide in the air from time to time. He considered that the proportion of carbon dioxide in the air was probably diminishing, although, of course, very slowly. "What," he asked, "will be the result?"

"Cet appauvrissement continue-t-il encore, et, s'il en est ainsi, ira-t-il jusqu'au point où il causerait la ruine de la végétation et par suite la fin de toute vie à la surface de la terre? La solution de cet problème d'un si haut intérêt nous échappe absolument. Elle ne pourra être donnée que par les générations qui viendront longtemps après nous."

Well may we envy a man and a generation that had nothing worse to worry about!

E. J. Russell.

ALFRED SENIER.

BORN JANUARY 24TH, 1853; DIED JUNE 29TH, 1918.

I.

ALFRED SENIER was born on January 24th, 1853, at Burnley, in Lancashire. His father, who had been one of the early settlers in Dover, Wisconsin, had returned to England some six years previously to engage in business as a pharmacist, but for reasons of health he found it necessary to return to America shortly after the birth of Alfred, his eldest son. Thus except for a brief visit to England during infancy and another during his student days, Senier's whole youth up to the time of his graduation as M.D. at the University of Michigan in 1874 was spent in the United States, chiefly at Mazomanie. Mr. Alfred Senier, the father, appears to have been a man of romantic disposition, which found its expression in a certain restlessness, leading him in early life to spend several years at sea and later to travel considerably in Europe. The son inherited this taste for travel, and was allowed to visit both London and Paris at the age of eighteen in the middle of his student career.

Immediately after his graduation the family finally returned to London, where Senier obtained a post at the school of the Pharmaceutical Society, first as assistant to Prof. Attfield and later as demonstrator. He was elected a Fellow of the Chemical Society in 1875 and a Fellow of the Institute of Chemistry three years later.

In 1881 he left the school of the Pharmaceutical Society in order to take charge of the chemistry teaching at St. John's College, Battersea, where he remained for three years.

During this period in London his interests extended beyond his professional duties, which hitherto did not seem to offer him sufficient scope for his mental activities. Endowed as he was with the faculty of accurate reasoning, and with clearness and breadth of mental vision, his interest at this time turned markedly to philosophical questions. We find him appointed as honorary secretary and treasurer of the Aristotelian Society on April 19th, 1880, when it was first organised. He acted in this capacity until 1884, and in 1902 he was elected an honorary life member. At its fifth meeting he delivered a lecture to the Society on "Plato." In 1882 we find him delivering a series of lectures on the "Elements and Early History of Terrestrial Physics" to the Positivist Society in Newton Hall, Fetter Lane. It is also interesting to observe that he wrote to the *Pharmaceutical Journal* in 1877 a spirited letter in

support of the proposal to admit lady pharmacists into the Pharmaceutical Society.

In 1884 he left London for Berlin, where he studied chemistry under A. W. von Hofmann. It was at this period of his life that he received his greatest inspiration. Enthusiastic and imaginative by nature, he threw himself wholeheartedly into his work, and soon attracted the attention of Hofmann, who became his ideal as a professor, lecturer, and teacher. A close friendship bound him to his old master, in whose family circle he spent many happy evenings, and whose personality made a lasting impression on his mind.

Later in life when fulfilling his duties in an academic chair he loved to think that the same happy relations existed between his students and himself as he had felt when a student of Hofmann. His interest in his past students never flagged. He was ever ready to help them, and always pleased to hear of their success.

Senier's own exceptional powers as a teacher were no doubt due to a large extent to the powerful influence of Hofmann, of whom he was never tired of speaking. Among his papers this idea is expressed in words thus: "I had special opportunities for studying the methods of teaching for which Hofmann was justly famous. He possessed that rare gift of inspiring his students with the discoverer's enthusiasm. We discovered, with him to lead us, things known to science; and then, without realising a difference, we followed him to things that were new, and thus became chemists with the habit of research. With such a leader in research, with such a teacher in the right meaning of the word, no wonder that those who came within his influence became inquirers and teachers too."

On June 25th, 1887, he graduated Ph.D. in Berlin, and returned shortly afterwards to London.

Here he remained for a few years writing articles for the standard dictionaries of chemistry until he was called to act as locum tenens for Maxwell Simpson, Professor of Chemistry at Queen's College, Cork, in 1890. The latter resigned the following year, and was succeeded by Prof. A. E. Dixon, of Galway. The vacancy thus created was filled by the appointment of Senier to the Chair of Chemistry at Galway, which he occupied until his death.

This Chair when first established in 1849 was filled by Edmund Ronalds, who in the early days of the Chemical Society served as Secretary and also acted as Editor of this Journal.

In addition to fulfilling the duties as Professor of Chemistry at Queen's College, Galway, Senier acted as Lecturer in Medical Jurisprudence and Hygiene.

In Galway his professorial duties, his work on the College Coun-

cil, and his personal interest in his students engaged his closest attention. His strong personality and buoyant enthusiasm made a powerful appeal to the minds of his students, with whom he was always immensely popular. He was a champion of students' interests, and never tired of reminding them that he was, and would remain, "always a student." Although not naturally attracted to athletic sports, he quickly realised their healthy influence and value in promoting *esprit de corps* and harmony among young men, assembled from all parts of Ireland, from homes representing all shades of religious and political differences. They sought and obtained in Galway a University training under a system which, although technically non-residential, was by reason of the smallness and isolation of the "Citie of the Tribes" virtually residential. Senier seized his opportunity and quickly won the affection of all the students by becoming the active patron of their sports. He founded the athletic union and acted as its president and treasurer for seventeen years. The astonishing prowess of the football team in its competitions with the larger sister colleges of Belfast and Cork was in no small measure due to his sympathetic and generous support.

Meanwhile, the problem of continuing his researches had to be faced, and was tackled courageously and successfully. At first little progress could be made, as Galway offered but a poor field for creating and maintaining an advanced chemical atmosphere. Nevertheless, he persisted in his attempt, and soon acquired a good chemical library and equipment sufficient to make a start. Well-furnished modern laboratories soon followed, and in conjunction with various assistants, demonstrators, and senior students he was eventually able to contribute a large number of papers, chiefly on acridines and on phototropic and thermotropic compounds, to the *Transactions* of this Society.

In 1908 the Royal University of Ireland conferred on him the degree of D.Sc. *honoris causa*. This event was made the occasion of a public presentation to him of an address and silver casket from his old students, whose eager and liberal response, even from the most distant parts of the world, bore ample testimony to the lasting feeling of reverence and goodwill in which they held their old teacher and patron of their sports.

He was elected a member of the Royal Irish Academy, and in 1912 he acted as President of the Chemical Section of the British Association at the Dundee Meeting.

When the National University of Ireland was created in 1908 he took an active part in its organisation and development. He was

a member of the Senate until his death, which took place on June 29th, 1918, in Galway after a brief illness. Senior married in 1887, and is survived by his wife and two daughters.

W. S. M.

II.

By the death of Alfred Senier the country has lost one of its most enthusiastic and devoted workers in the domain of organic chemistry. The loss is felt most keenly by all his students and co-workers, who will always cherish the remembrance of his sympathetic and inspiring personality. In him the spirit of scientific inquiry was strong indeed, for in the face of difficulties, which would have baffled and beaten many a man of less sterling worth, his courage never failed, but enabled him to pursue unwearyingly the lofty ideals which he had formed in his youth and to achieve a measure of success and distinction which will assuredly become fruitful in the future.

Even before leaving America he had shown evidence of a desire to undertake original investigations, his first paper, on the analysis of soap, appearing in the *American Journal of Pharmacy* in 1874. At the School of the Pharmaceutical Society his aspirations received encouragement from Prof. Attfield, and he contributed a series of articles to the *Pharmaceutical Journal*, chiefly relating to the investigation of pharmaceutical preparations and including a table for the qualitative analysis of scale preparations, alkaloids, etc. The interaction of glycerol and borax particularly engaged his attention, because he found that he could utilise it as a means for detecting glycerol. In 1878 he contributed to the *Transactions* of the Chemical Society "A New Test for Glycerin." He also published a number of articles in the *Sanitary Engineer*.

In Berlin Senier came under the powerful influence of A. W. von Hofmann. The enthusiasm which Hofmann aroused in him remained with him to the end, and he spoke of him almost with veneration in his public lectures.

Inspired as he was by his experience in Germany, the whole course of Senier's later life afforded abundant evidence that he had learned nothing of the modern German aggressive spirit of world-domination. Indeed, his realisation of its existence only came to him after war was declared, and its effect on him was painful in the extreme, as shown in his letters to the writer.

In Berlin his attention was first directed to the action of heat on the formyl and thioformyl derivatives of aromatic amines, and later to the investigation of cyanuric acid and cyanuric chloride. He was

able to show that the alleged α- and β-isomerides obtained by Herzig by the interaction of carbamide and hexabromoacetone were in reality identical with ordinary cyanuric acid. This work was embodied in his dissertation for the degree of Ph.D.

Shortly after his appointment to Galway he reverted to the examination of cyanuric acid, and found that the white solid produced by the polymerisation at 0° of freshly distilled cyanic acid was not pure cyamelide as was supposed, but consisted chiefly of cyanuric acid mixed with 30 per cent. of cyamelide.

Being greatly interested in all Hofmann's work, he decided to follow up the reaction by which ethylenediamines and piperazines are formed from arylamines. By using methylene dihaloids instead of ethylene dihaloids, he found that although the simplest arylamines give rise to methylenediamines, as the molecules increase in complexity through the inclusion of methyl groups or of condensed rings, the character of the reaction changes and results in the formation of acridines. Thus from ψ-cumidine he obtained hexamethylacridine, and from α-naphthylamine a new dinaphthacridine. This result led him to study the subject of acridines in some detail, and a series of papers appeared in the *Transactions*. He also introduced a new and convenient system of notation in the acridine series. This work was followed by a paper on quinazolines and a series of papers on the synthesis of phototropic compounds, to which he was led by his observations on salicylidene-*m*-toluidine during the course of his investigations on acridines. This discovery of phototropic change led him to prepare and examine a large number of similarly constituted anils, many of which were also phototropic, although the property was by no means characteristic of the class. The change from the paler variety to the darker under the influence of sunlight occurs rapidly in a few minutes—whereas the reverse change requires a much longer time. This process of reversal can, he found, be accelerated by raising the temperatures, but there appears to be for each substance a critical temperature above which the property of phototropic change disappears. In some cases this temperature is near the melting point; in others it is much lower; in fact, in the case of two compounds examined, namely, salicylidene-*p*-anisidine and 2-hydroxy-3-methoxybenzylidene-*p*-xylidine, no phototropic change is observed until a temperature of $-20°$ is reached. Similar colour changes were observed to take place under the influence of heat instead of light, this phenomenon being termed *thermotropy* by Senier. Thermotropy appears to be much commoner than phototropy, and in many instances the thermotropes were also found to be phototropic. The suggestion was put forward by Senier that these phototropic and thermotropic

changes are to be ascribed to isomeric changes affecting the aggregation of molecules in solids rather than to changes in the structures of the molecules themselves. In his Presidential address to Section B of the Dundee meeting of the British Association in 1912 he developed this idea of the existence of solid molecular aggregates. Several instances of polymorphic changes due to trituration were also examined, chiefly in the case of *p*-hydroxybenzylidenearylamines. This work, extending over several years, was the subject of a series of papers in the *Transactions*, and remains unfinished. No doubt it will be possible in the future to throw more light on the subject by means of optical measurements.

Apart from his purely scientific studies, Senier took a deep interest in educational affairs. The difficulties which had to be encountered in Galway were due partly to the remoteness of the College from the main centre of scientific activity and partly to the anomalous character of the College during the greater part of Senier's life in Galway.

Since the dissolution of the Queen's University in 1879 the three Colleges at Belfast, Galway, and Cork had been reduced from the status of integral members of a university to that of colleges where students were able to study for the examinations of an external institution—the Royal University. In addition to this loss of prestige, the College at Galway suffered through lack of active support by the people of Connaught. It was therefore not in close sympathy with its environment. This state of affairs has happily been remedied by the abolition of the Royal University and the creation in 1908 of two new teaching universities, namely, the National University of Ireland and the Queen's University of Belfast. The College at Galway, re-named "University College, Galway," became a constituent part of the National University, and Senier was elected to a seat on the Senate. The existence of the College has often been threatened, but it has survived and, indeed, attained a flourishing condition. There is no doubt that Senier's efforts to foster the spirit of scientific research materially advanced the cause of education in Galway and in Ireland. In his public lectures on "A Visit to Giessen; or Thoughts on Liebig and Chemistry in Germany" and "Bonn on the Rhine; Pages from its History and Stray Thoughts on Education" he deals in a very attractive way with the history of the development of scientific research in Germany, and in his lecture before the Royal Dublin Society in 1910 on "The University and Technical Training" he made a very lucid and careful analysis of the various university systems in the world. In view of modern needs these essays* are

* Published at Dublin, 1910, by Edward Ponsonby, 116, Grafton Street.

well worth reading, for he explains very clearly how industrial development does not depend on the technical education of the operatives, but arises naturally from the development of the highest form of scientific activity at the universities.

P. C. AUSTIN.

JOHN BISHOP TINGLE.

BORN 1867; DIED AUGUST 5TH, 1918.

JOHN BISHOP TINGLE, Professor of Chemistry in McMaster University, Toronto, who died on August 5th, 1918, at the age of fifty-one, after a brief illness, received his early training at the Royal Grammar School, Sheffield, entering Owen's College, Manchester, in 1884, under the late Sir Henry Roscoe. In 1887 he proceeded to the University of Munich to study with Claisen and von Baeyer, where he took the degree of Doctor of Philosophy in 1889. While at Munich his studies were essentially in organic chemistry, his dissertation for the degree dealing with the action of ethyl oxalate on aliphatic ketones.

On returning to England Dr. Tingle held certain junior appointments which offered him opportunities for research. Owing, however, to unforeseen family responsibilities he was compelled to give up, for a time, his chosen career of investigation, and taught chemistry in secondary schools.

In 1896 he came to America and was successively professor of chemistry at the Lewis Institute, Chicago (1897–1901), Illinois College, Jacksonville (1901–1904), and assistant in charge of organic chemistry at Johns Hopkins University under Professor Remsen (1904–1907). During his residence in the United States Dr. Tingle became sub-editor and abstractor in organic chemistry on the staff of the *American Chemical Journal*, his work being characterised with care and precision, and as his study of current literature in his chosen field was extensive and exhaustive he spared no pains to make his abstracts clear, complete, and useful. His long training as an abstractor on the staff of the Journal of the Chemical Society specially qualified him to take this important part in organising the organic abstracts for the American journal.

Dr. Tingle was appointed professor of chemistry at McMaster University, Toronto, in 1907, in which post he laboured energetically and faithfully until his death. It was perhaps in teaching, for which he possessed a special talent, that Dr. Tingle did his best

and most valuable work for the country of his adoption. He was insistent on the importance of careful, accurate, and clean craftsmanship, and held that theory was useless and often misleading without a knowledge of how it had been deduced and how it could be applied in practice. He laid special stress on the need of manipulative skill of the highest order as a necessary pre-requisite to orderly and clear reasoning and successful results.

Dr. Tingle's original work, embodied in upwards of thirty publications, deals with problems of organic chemistry, and is centred chiefly round the mechanism of the "Claisen reactions" and the products and mechanism of nitration in the benzene series. His last paper, which did not appear in print until after his death, settled certain minor points previously undetermined, and was intended to clear the way for a comprehensive study of the laws governing nitration and the means by which their reactions could be controlled. Dr. Tingle made organic research his life work, and carried through to a successful issue a large number of investigations in his chosen field. He held a first place among organic chemists in Canada, and had he been spared it was expected that he would have been able in a few years to devote himself almost exclusively to research. Much has been lost by his death.

In the sphere of Canadian war work Dr. Tingle was the first to recommend the intensive training of girls for employment in munition and chemical factories in Canada, and laid himself out energetically to instruct them towards this end. The extra work involved undoubtedly accelerated his death.

He translated and edited several important works in chemistry. For a long time "Spectrum Analysis," by Landauer and Tingle, was the most comprehensive work on the subject in English.

Dr. Tingle was a kind and generous man, taking a great personal interest in his students and their work and exciting their ambition and enthusiasm for advanced study.

He leaves a widow and two children.

W. R. L.

Organic Chemistry.

The Influence of Catalysts on the Chlorination of Hydrocarbons. V. R. Kokatnur (*J. Amer. Chem. Soc.*, 1919, **41**, 120—124).—Attempts were made to prepare pentachloroethane by the limited chlorination of *s*-tetrachloroethane. Various catalysts, such as vegetable and animal charcoal and metallic iron, were suspended in *s*-tetrachloroethane, and chlorine gas was passed through the liquid at various temperatures. In no case was pentachloroethane found among the products of the reaction, which consisted only of hexachloroethane and unchanged tetrachloroethane. In other trials, chlorination was effected by heating with bleaching powder and water and with anhydrous aluminium chloride. In these cases, also, hexachloroethane only was produced, although a certain amount of the tetrachloroethane was converted into *as*-tetrachloroethane. It is not decided whether this complete chlorination, giving hexachloroethane as the only product, is to be ascribed to the influence of catalysts or to the symmetrical structure of the tetrachloroethane, whereby both atoms of hydrogen are equivalent in function and are therefore substituted simultaneously. It is true that pentachloroethane may be produced by chlorinating in the presence of actinic light, but that may be due to the specific influence of the light on the constitution either of the *s*-tetrachloroethane, making it unsymmetrical, or of the chlorine molecule.

J. F. B.

Constitution of the Product of the Action of Acetylene on Mercuric Chloride. W. Manchot (*Annalen*, 1918, **417**, 93—106. Compare Manchot and Haas, A., 1913, i, 1009).—A reply to Biltz and Reinkober's criticisms of the author's formula,

$$C_2Hg,HgCl_2,HgCl,H_2O.$$

[With Franz Mährlein.]—Styryl ethyl ether and an aqueous solution of mercuric acetate (3 mols.) are warmed at 50°, the cooled liquid is poured, after two hours, into a 10% solution of sodium chloride, whereby a white *substance*, $CHPh\!:\!CH\cdot OH,2HgCl\cdot OH$, is obtained. It melts partly at about 120°, decomposes somewhat violently when heated over a free flame, is scarcely attacked by dilute sodium hydroxide solution, and yields phenylacetaldehyde by heating with hydrochloric acid.

In view of the preceding observations, the author now inclines to the opinion that the product of the action of acetylene on mercuric chloride, Biltz and Mumm's "trichloromercuriacetaldehyde," is an additive product of vinyl alcohol; a formula is not recorded, on account of the uncertainty of the individual character of the substance.

C. S.

Constitution of Geraniol, Linalool, and Nerol. ALBERT VERLEY (*Bull. Soc. chim.*, 1919, [iv], **25**, 68—80).—α-Citral when boiled with 1% aqueous sodium hydroxide gives *β-methyl-Δ^α-heptenone*, $CH_2:CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe$, b. p. 168°, which when oxidised with potassium permanganate gives the glycol, $HO\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe$, which when oxidised with chromic acid only gives traces of acetone. β-Methyl-Δ^{α}-heptenone when warmed on a water-bath with dilute sulphuric acid is readily transformed into its Δ^{β}-isomeride, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot COMe$ (compare Tiemann, *Ber.*, 1895, **28**, 21, 2126). From these facts, the author assigns to geraniol, obtained by the reduction of citral, the constitution $CH_2:CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe:CH\cdot CH_2\cdot OH$, which corresponds with citronellol. With hydrogen bromide, this geraniol gives a tribromo-compound,

$$CH_3\cdot CMeBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMeBr\cdot CH_2\cdot CH_2Br,$$

which by treatment with alkali yields iso*linalool*, b. p. 200—207°, which thus has the constitution

$$CMe_2:CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH:CH_2,$$

ordinarily assigned to linalool, which must, therefore, be represented by the formula $CH_2:CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH:CH_2$. With hydrogen iodide, geraniol gives a monoiodo-derivative, which under the influence of alcoholic sodium hydroxide readily loses hydrogen iodide, giving a quantitative yield of nerol, to which the author assigns the constitution

$$CMe_2:CH\cdot CH_2\cdot CH_2\cdot CMe:CH\cdot CH_2\cdot OH,$$

previously attributed by Tiemann to geraniol. Nerol when oxidised with dilute chromic acid mixture gives *neral*, b. p. 120°/20 mm., D 0·890, which is easily decomposed by alkalis, giving acetaldehyde and β-methylheptenone, and with an alkaline solution of cyanoacetic acid yields *nerylidenecyanoacetic acid*, m. p. 95°.

Of the substances of the geranic series occurring in nature, geraniol, citral, linalool, and methylheptenone, there exist two isomeric forms, α and β, of which the α-form is much the more abundant of the two, being accompanied by only a very small proportion of the β-form.

The new formula for geraniol given above permits of a ready explanation of the close relationship which exists between geraniol and dipentene, $CH_2:CMe\cdot CH{<}{\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2-CH\end{smallmatrix}}{>}CMe$. W. G.

Molecular Transpositions of α-Glycols. I. Introduction. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 9—19).—A theoretical discussion in which the author shows that Werner's theory (A., 1906, i, 436) combined with that of Tiffeneau (A., 1906, i, 724) can be successfully applied to the interpretation of the phenomena of the transpositions occurring in the dehydration of α-glycols. He attributes to each radicle an "aptitude for migration," or a "relative mobility" and a "saturation capacity" which vary with the different radicles, but in the same sense, and assumes that these control the transpositions, according to which he shows

that the symmetrical and asymmetrical isomeric glycols give the same products of dehydration:

$$HO\cdot CRR'\cdot CRR'\cdot OH \longrightarrow R'\cdot CO\cdot CR_2R' \longleftarrow HO\cdot CR_2\cdot CR'_2\cdot OH.$$

These transpositions may, however, be modified by the nature of the dehydrating agent, and in the case where R or R′ is a phenyl group by the introduction of substituents into the benzene nucleus. The benzyl group apparently has a smaller "mobility" and a smaller "capacity of saturation" than the phenyl group. W. G.

Preparation of Methyl Sulphate. WALTER NORMAN HAWORTH and JAMES COLQUHOUN IRVINE (Brit. Pat., 122498).—For the production of methyl sulphate, dimethyl ether and sulphur trioxide are caused to combine directly in the presence of a solvent. The sulphur trioxide may, if desired, be employed in the form of the dilute gas produced by the reaction of sulphur dioxide with air by the contact process. Both the sulphur trioxide and the methyl ether vapours must be perfectly dry, and the latter must be free from the vapours of alcohol. The two gases are passed simultaneously in approximately equimolecular proportions into the solvent liquid, which may conveniently consist of methyl sulphate itself. The mixture is stirred continuously and cooled by a water-jacket or coil. The methyl sulphate produced is drawn off and treated with iron filings or other reducing agent to neutralise the influence of any excess of sulphur trioxide which may be present; it is then purified by rectification under diminished pressure.

J. F. B.

Preparation of Acetic Acid from Acetylene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 297442; from *Chem. Zentr.*, 1919, ii, 61).—Acetylene is treated with solutions of hydrogen peroxide, persulphuric acid or monopersulphuric acid, or solutions or suspensions of their salts in acids in the presence of mercury or mercury compounds. Thus a quantitative yield of acetic acid is obtained in a single operation when acetylene is treated with solutions or suspensions of persulphates in water or acids in the presence of mercury or mercury compounds. Salts of monopersulphuric acid, solutions of persulphuric acid and monopersulphuric acid, and of hydrogen peroxide may also be used; in place of the latter, any substance (percarbonates, peroxides) may be employed which yields hydrogen peroxide when acidified. H. W.

Manufacture of Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat., 112765).—The reaction between acetylene and glacial acetic acid for the production of ethylidene diacetate is caused to take place in the presence of aromatic or aliphatic sulphonic acids and mercuric acetate, and in the absence of mineral acids or acid salts of mineral acids. The formation of tarry by-products and the secondary decomposition of the ethylidene diacetate are thereby suppressed. Suitable acids are benzene-

sulphonic, naphthalenesulphonic, camphorsulphonic, sulphoacetic methionic acids, etc. Forty parts of mercuric oxide are dissolved in 200 of glacial acetic acid, a solution of 50 parts of β-naphthalenesulphonic acid in 200 of glacial acetic acid is added at 70°, and the mixture is caused to absorb 200 parts of acetylene during two hours at 70°. The excess of acetic acid is then separated from the ethylidene diacetate in the usual way. J. F. B.

Preparation of the Bromo*iso*valeric Ester of Bromoamylene Hydrate. EMIL RATH (D.R.-P. 309455; from *Chem. Zentr.*, 1919, ii, 61).—The *ester* is obtained as a pale yellow oil of faint, characteristic odour, which can be distilled in a vacuum by heating a molecular mixture of bromoamylene hydrate and bromo*iso*valeryl bromide in the presence of an indifferent solvent at the temperature of the water-bath until hydrogen bromide ceases to be evolved; bromo*iso*valeryl chloride may be used in place of the corresponding bromide. H. W.

Theory of Acids. O. HINSBERG (*J. pr. Chem.*, 1918, [ii], 98, 145—154).—Elaborating the conception of multiple valency centres (A., 1917, ii, 173, 461; 1918, ii, 106), the author endeavours to correlate the acid properties of ethyl acetoacetate, oxy-acids, acetylene, hydrogen cyanide, hydrogen sulphide, and the halogen acids. Acids are compounds which contain hydrogen bound either alone (HCl; H_2S) or with other elements (oxy-acids; ethyl acetoacetate; hydrogen cyanide) to an element of groups V—VII of the periodic table. The acidic hydrogen atom is linked to one atom by a principal valency and to other atoms by several subsidiary valencies, the effect of this competition of forces being to render the hydrogen atom mobile.

The mobility and loose binding of the hydrogen atom within the acid molecule may be regarded as the preliminary condition for dissociation into anion and cation. C. S.

Nitration of Sucrose: Sucrose Octanitrate. E. J. HOFFMAN and V. P. HAWSE (*J. Amer. Chem. Soc.*, 1919, **41**, 235—247).—After removal of acid, the product of the nitration of sucrose by sulphuric and nitric acids in the cold forms a tough, viscous, semi-transparent, slightly hygroscopic mass, which can be pulverised to a sticky, white powder when hardened by cooling. When heated and allowed to cool, it begins to flow sluggishly at 40° and then gradually sets, until at 8° it becomes very hard and brittle. When acid-free, it is fairly stable, and may be kept without appreciable change for weeks at the ordinary temperature, but it decomposes when heated at comparatively low temperatures, this decomposition becoming more rapid after long heating; it is very sensitive to friction or impact. The mean nitrogen content of different preparations was 15%, the molecular weight in freezing acetic acid, benzene, or nitrobenzene, 428·9—565·2, and the specific rotation using light from a frosted tungsten lamp filtered through 6% dichromate solution, $[\alpha]^{20}$ +56·66°.

Sucrose octanitrate, $C_{12}H_{14}O_3(NO_3)_8$, obtained by evaporation of the alcoholic solution of the above product at the ordinary temperature, forms elongated, acicular crystals, probably of the monoclinic, but possibly of the orthorhombic, system [HERBERT INSLEY], m. p. 85·5°, $[\alpha]^{20}$ +56·05°; it has the normal molecular weight in freezing nitrobenzene, and when heated gradually from 33° to 87° in a period of nearly two hours it shows no signs of decomposition. Photomicrographs of the crystals are given. Sucrose octanitrate may be estimated in explosive mixtures by means of its rotatory power and nitrogen content (15·95%). T. H. P.

Preparation of Soluble Starch. JAMES CRAIG SMALL (*J. Amer. Chem. Soc.*, 1919, **41**, 113—120).—Starch may be entirely converted into soluble starch, without the formation of erythrodextrin or other cupric reducing products, by boiling with alcoholic hydrochloric acid under carefully regulated conditions. These conditions have been studied, and the method adopted by the author consists in suspending 20 grams of starch in 100 c.c. of 95% alcohol, adding 0·75 c.c. of strong hydrochloric acid (D 1·19), and boiling for exactly ten minutes with continuous agitation. The conversion is stopped by adding all at once the previously determined quantity of sodium hydrogen carbonate solution necessary to neutralise the acid. The soluble starch is then washed several times with alcohol by decantation, collected on a filter, and dried. The experiments performed in establishing the conditions of the above method of preparation showed that the amount of hydrolysis bears a direct ratio to the concentration of the hydrogen ion, but it would appear that in favourable circumstances the complete conversion into soluble starch constitutes a definite stage preliminary to further hydrolysis, and that maltose is not split off from the starch molecule as a direct consequence of this change. This supports the idea that soluble starch is a hydrated starch. From soluble starch onwards, the hydrolysis again appears to bear a direct ratio to the acid concentration. J. F. B.

Relations between the Viscosity of Cellulose Nitrate Solutions and the Nitration Process, with Special Reference to Wood Cellulose. G. LEYSIEFFER (*Koll. Chem. Beihefte*, 1918, 10, 145—178).—The material employed was a chemically pure wood cellulose prepared from deal. It contained α-cellulose 80·4, β-cellulose 6·8, γ-cellulose 12·8%. The ash amounted to 0·20% and the fat to 0·44%. The nitration with a mixed acid of known composition was performed much in the usual manner; both cold and hot washing were employed. The drying was effected at 36—40° for twenty-two hours. The nitrogen content of the product was estimated by the Schulze-Tiemann method, and the nitrates were further characterised by solubility determinations in alcohol or ether-alcohol (2:1). The viscosity of the acetone solutions of the nitrates was determined by the Ost viscosimeter.

As the results of a large number of experiments, tables and

graphs of which are given, the following conclusions are drawn: (1) By the nitration of cellulose, the same value for the viscosity is always obtained provided all the factors which influence the internal friction (composition of the nitrating acid, temperature of the bath, duration of the nitration, proportion by weight of cellulose to acid, method of preparation and properties of the cellulose employed) are kept constant. (2) The greater the nitric acid content of a nitrating acid, the higher is the viscosity of the nitrated cellulose in acetone solution. If, however, the percentage content of nitric acid equals or exceeds that of the sulphuric acid, smaller values are found for the internal friction. This diminution is more marked in the case of dilute nitrating acids than of concentrated nitrating acids. Increasing the water content from 0% to about 11% causes an increase of the viscosity, only, however, if the nitric acid content is less than the sulphuric acid content; otherwise, and if the water content exceeds the above limit, smaller values are obtained for the viscosity. (3) Nitration at temperatures below 0° produces nitrates having high viscosity values. The higher the temperature of nitration, the smaller is the viscosity. (4) The viscosity values vary considerably in the case of nitrates which have been nitrated for only a short time (five to thirty minutes). They increase so long as the nitrogen content increases, but prolonged action of the nitrating acid results in a diminution of the viscosity. (5) A close connexion is found between the nitrogen content of a cellulose nitrate and the internal friction of its acetone solution: the higher the nitrogen content, the higher is the viscosity. (6) Acetone solutions of cellulose nitrates become more mobile with keeping, strongly viscous solutions more so than less viscous solutions. (7) The kind, method of preparation, and previous treatment of a cellulose are of great influence on the viscosity. A high content of γ-cellulose causes increased viscosity in the nitrate. Nitrates from cotton cellulose show higher viscosities than those from wood cellulose. C. S.

The *n*-Butylarylamines. III. Constitution of the Nitro-derivatives of *n*-Butyl-*p*-toluidine. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1919, **115**, 175—181).

Amino-acids. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1918, 12, 290—317).—By using a new method of extraction, the author has isolated a new aminohydroxy-acid and a new peptide from the products of acid hydrolysis of caseinogen.

When caseinogen is hydrolysed with sulphuric acid, and the latter subsequently removed as barium sulphate, on submitting the neutral concentrated solution of amino-acids to continuous extraction with butyl alcohol, it is found that five fractions can be obtained, as follows: (1) Monoamino-acids, both aliphatic and aromatic, which, although insoluble in butyl alcohol, are extracted in the above process, but deposited as a cream-coloured, granular powder in the extraction flask. (2) Proline, soluble in alcohol and extracted by

butyl alcohol. (3) Peptide anhydrides (diketopiperazines), extracted by butyl alcohol, but separated from (2) by their sparing solubility in alcohol or water. (4) Dicarboxylic acids, not extracted by butyl alcohol. (5) Diamino-acids, not extracted by butyl alcohol, but separable from (4) by phosphotungstic acid and other means. It is noteworthy that no indications of racemisation of the products during this process have been observed, and materially higher yields of many amino-acids were obtained than by existing methods. The fact that the monoamino-acids, which are essentially insoluble in all alcohols, are extracted by butyl alcohol under the above conditions, is due to the passage of a certain amount of water into the alcohol, since the extraction is very unsatisfactory if the aqueous solution of amino-acids contains an excess of salts, such as calcium chloride.

Using this method, the author found as an average of five determinations 8·0% proline from caseinogen, and from his specimen he prepared l-*prolylhydantoin*, $CH_2<\begin{matrix}CH_2\cdot CH\cdot CO\\ CH_2\cdot N—CO\end{matrix}>NH$, m. p. 165—167°, $[\alpha]_D^{20}$ −232° to −238·5°, by passage through the uramido-acid.

The method of extraction with butyl alcohol furnishes a ready means of obtaining a dry, almost neutral amino-acid mixture, which would serve as a basis for nutrient media with or without the addition of tryptophan, and might possibly find use for dietetic purposes, since most of the amino-acids which furnish dextrose in the diabetic organism are absent.

After the precipitation of the diamino-acids from the amino-acids not extracted by butyl alcohol, and subsequent separation of glutamic and aspartic acids, the former as its hydrochloride and the latter by the method of Levene and Van Slyke (compare A., 1910, i. 719), using freshly precipitated lead hydroxide, it was found that large amounts of at least one other dicarboxylic acid were still present, and it could be isolated. This acid, isolated through its silver salt, was characterised as *β-hydroxyglutamic acid*, $CO_2H\cdot CH(NH_2)\cdot CH(OH)\cdot CH_2\cdot CO_2H$, crystallising in stout prisms. It is optically active and extremely soluble in water. It yielded *silver, copper, mercury, lead, cadmium, zinc, calcium*, and *barium* salts, gave a diethyl ester, and on prolonged heating at 100—110° over phosphorus pentoxide lost a molecule of water, giving a *compound*, $CO<\begin{matrix}NH—CH\cdot CO_2H\\ CH_2\cdot CH\cdot OH\end{matrix}$. On heating the acid with zinc dust, an intense pyrrole reaction was obtained, and when reduced with fuming hydriodic acid at 150° it yielded glutamic acid, amongst other products. The sodium salt of the acid (1 mol.) when oxidised with chloramine-T (1 mol.) gave an *aldehyde*, $C_4H_6O_4$, which with *p*-nitrophenylhydrazine gave a characteristic *osazone*, $CO_2H\cdot CH_2\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot CH:N\cdot NH\cdot C_6H_4\cdot NO_2$, m. p. 297—299°, giving a red *ammonium* salt. With potassium cyanate. β-hydroxyglutamic acid yielded a uramido-acid, which when heated with acids gave a very soluble hydantoin. The acid gave derivatives

with phenylcarbimide and β-naphthalenesulphonyl chloride, which were not well defined. It also gave characteristic colour reactions with various phenols and concentrated sulphuric acid.

The peptide mixture, extracted by the butyl alcohol from the products of hydrolysis of the caseinogen, was separated from proline, and obviously consisted of a number of different compounds. A tyrosine-containing peptide was isolated, but not identified, and also a peptide, which was shown to be d-*iso*leucyl-d-valine *anhydride* [*iso*propyl-*sec*.-*butyldiketopiperazine*],

$$CHMe_2\cdot CH<{CO\cdot NH \atop NH\cdot CO}>CH\cdot CHMeEt,$$

m. p. 310—312°, $[\alpha]_D^{20}$ $-42\cdot0°$ to $-43\cdot5°$. W. G.

Formation, by Oxidation, of Organic Substances, of an Intermediate Substance spontaneously producing Carbamide. R. Fosse (*Compt. rend.*, 1919, **168**, 320—322).—The author shows that whereas, by oxidation with potassium permanganate, substances such as casein and amino-acids give only a small yield of carbamide, if the oxidised solution is subsequently heated with aqueous ammonium chloride, a very much greater yield of carbamide is obtained. Similarly, if substances such as glycerol, carbohydrates, or formaldehyde are oxidised with potassium permanganate in the presence of ammonia, the yield of carbamide is practically negligible, but if the products are heated with aqueous ammonium chloride, a considerable yield of carbamide is obtained. W. G.

The Action of Chlorine on Hydrazine, Hydroxylamine, and Carbamide. C. T. Dowell (*J. Amer. Chem. Soc.*, 1919, **41**, 124—125).—When a large excess of chlorine is allowed to react with hydrazine and hydroxylamine in contact with carbon tetrachloride, evidence is obtained showing the formation of nitrogen trichloride, since on separating the carbon tetrachloride and treating it with a solution of potassium iodide, nitrogen is evolved. The author has confirmed the observations of Chattaway on the properties of dichlorocarbamide, in that when kept its solution is decomposed, giving as one of the products nitrogen trichloride. Chattaway considered that in the course of this decomposition carbon dioxide and monochloroamine were formed, the latter giving ammonia and nitrogen trichloride. The author, however, has tested the solution for monochloroamine by Raschig's test with ammonia and benzaldehyde, whereby, owing to the formation of hydrazine, the insoluble benzaldazine should be produced. This is not the case, and no evidence of monochloroamine is obtained. It is suggested that the nitrogen trichloride may be formed by the action of chlorine, which may also be a decomposition product of dichlorocarbamide. J. F. B.

Coal. Amé Pictet (*Ann. Chim.*, 1918, [ix], **10**, 249—330).—A more detailed account of work already published (compare A., 1911, i, 850; 1913, i, 1315; 1914, i, 155; 1915, i, 512; 1916, i, 800; 1917, i, 515). W. G.

Halogenation. XVIII. Direct Iodination by means of Iodine and Nitric Acid. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1919, **41**, 292—295).—In continuation of the investigations on iodination by nitric acid (A., 1917, i, 332), it is found that the reaction takes place readily in the case of aromatic acids and aromatic haloid derivatives. Thus, iodobenzene gives a good yield of *p*-di-iodobenzene. Although a small proportion of trinitrophenol is formed as a result of the hydrolysis of iodobenzene and simultaneous nitration in presence of nitric acid (*loc. cit.*), it is not possible to prepare trinitrophenol catalytically by using a small quantity of iodine with continued addition of benzene and nitric acid, since iodobenzene is quite stable under these conditions, any excess of iodine yielding *p*-di-iodobenzene, and any excess of nitric acid, *p*-iodonitrobenzene. The latter is, however, formed by the prolonged action of iodine and nitric acid on benzene, since *p*-di-iodobenzene is decomposed by nitric acid, giving *p*-iodonitrobenzene, a good yield of which may be rapidly prepared by this method of exhaustive iodination of benzene with repeated additions of iodine and nitric acid; the water accumulating on account of the decomposition of nitric acid must be removed from time to time.

On iodination with the required quantity of iodine and nitric acid, iodobenzene gives *p*-di-iodobenzene; chlorobenzene gives *p*-chloroiodobenzene, and bromobenzene, *p*-bromoiodobenzene. *p*-Chloro- and *p*-bromo-toluenes give *p*-chloro- and *p*-bromo-benzoic acids respectively, the methyl groups being oxidised to carboxyl and no entry of iodine taking place. From benzoic acid, *m*-iodobenzoic acid was obtained, and from *o*-phthalic acid, 4-iodo-*o*-phthalic acid. Phenylacetic acid gives *p*-iodophenylacetic acid and cinnamic acid, *p*-iodocinnamic acid. Salicylic acid yields trinitrophenol quantitatively, the carboxyl group being detached, and complex hydroxy-acids, such as tannin, give a small quantity of trinitrophenol; the latter is frequently obtained in traces on iodination of the aromatic acids. T. H. P.

Meta-substituted Aromatic Selenium Compounds. FRANK LEE PYMAN (T., 1919, **115**, 166—175).

Preparation of Monomethylaniline. PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and NOEL ALBERT NICHOLLS (T., 1919, **115**, 198—205).

Preparation of "Metol" (*N*-Methyl-*p*-aminophenol Sulphate). ROLLA N. HARGER (*J. Amer. Chem. Soc.*, 1919, **41**, 270—276).—In view of the comparative cheapness of quinol and also of methylamine when prepared by the methylation of ammonium chloride by means of formaldehyde (compare Werner, T., 1917, **111**, 844; Jones and Wheatley, A., 1918, i, 527), the author has made experiments on the preparation of "metol" by heating quinol and methylamine together under pressure. The

results obtained show that a lower temperature, and consequently a very much lower pressure, and a much shorter period of heating than those given in the Merck specifications (A., 1913, i, 1057), are the conditions under which the reaction should be carried out; a yield of 73% is obtainable.

N-Methyl-*p*-aminophenol sulphate begins to char at 245° and has m. p. 250—260° (decomp.). It crystallises in microscopic, six-sided, prismatic needles with roof-like ends. Addition to its solution of mercuric acetate solution results in the gradual development of an intense purple coloration, which may probably serve for the colorimetric estimation of "metol." T. H. P.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. III. Nitric Acid Derivatives of Chlorinated *o*-Cresols. TH. ZINCKE and O. PREISS (*Annalen*, 1918, **417**, 191—235. Compare Zincke and Pfaffendorf, A., 1912, i, 964; Zincke and Janney, A., 1913, i, 853).—The following new chloro-derivatives of *o*-cresol have been prepared. 4-Chloro-*o*-toluidine, by chlorination at 0° in glacial acetic and concentrated hydrochloric acids yields a *hexachloro-1-methyl*cyclo*hexene-2-one*, $C_7H_4OCl_6$, stout needles or prisms having a strong camphor-like odour, m. p. 105°, which is reduced in boiling alcoholic solution by tin alone to 3:4:5-*trichloro-o-cresol*, long needles, m. p. 77° (*acetyl* derivative, needles, m. p. 45°); if concentrated hydrochloric acid is also present, or if the reduction is effected by stannous chloride, tetrachloro-*o*-cresol is also produced. 3:5:6-*Trichloro-o-cresol*, needles, m. p. 62° (*benzoyl* derivative, needles, m. p. 110°), is prepared in a similar way from the keto-hexachloride obtained from 6-chloro-*o*-toluidine (Zincke and Pfaffendorf, *loc. cit.*). 4:5-*Dichloro-o-cresol*, needles, m. p. 101° (*benzoyl* derivative, needles, m. p. 80—81°), is obtained by leading the calculated quantity of chlorine into a chloroform solution of 4-*chloro-o-cresol*, needles, m. p. 73—74° (*benzoyl* derivative, leaflets, m. p. 53—54°), which is itself prepared from 4-chloro-*o*-toluidine.

3:4:5-*Trichloro-o-cresolnitroquinitrol*,

$$NO_2\cdot O\cdot C(OH){<}{\begin{matrix}CMe{=\!=}CH\\CCl(NO_2)\cdot CCl\end{matrix}}{>}CCl,$$

colourless, rhombic crystals, m. p. 105—106° (decomp.), obtained by adding 3:4:5-trichloro-*o*-cresol gradually to nitric acid, D 1·48, is converted into 3:4:6-trichloro-*p*-toluquinone by warm concentrated sulphuric acid, and is reduced (*a*) by stannous chloride, in cold dilute hydrochloric solution to 3:4:5-trichloro-*o*-cresol (a reduction of this kind cannot be effected with the corresponding tribromo-derivative, *loc. cit.*), (*b*) in methyl-alcoholic solution at 0° to 4:5-*dichloro-3-nitro-o-cresol*, yellow needles, m. p. 69° (*acetyl* derivative, rhombohedral crystals, m. p. 93—94°), and (*c*) in concentrated hydrochloric acid to 4:5-*dichloro-3-amino-o-cresol*, colourless leaflets, m. p. 161° (*hydrochloride*, leaflets; *diacetyl* derivative, needles, m. p. 194°; *triacetyl* derivative, leaflets, m. p. 126°), which is also obtained by the reduc-

tion of the preceding nitro-compound. The constitutions of these compounds are determined by the fact that the amino-compound can be converted into 4:5:6-trichloro-2:3-dihydroxytoluene.

By boiling with tetrachloroethane, 3:4:5-trichloro-*o*-cresol-nitroquinitrol is converted into 4:5-*dichloro-o-toluquinone* 2-*nitrate*, $NO_2\cdot O\cdot C(OH){<}{\substack{CMe{:}CH \\ CO{-}CCl}}{>}CCl$, yellow needles, m. p. 144° (decomp.), which is reduced by stannous chloride to 4:5-*dichloro*-2:3-*dihydroxytoluene*, needles, m. p. 107° (*diacetyl* derivative, needles, m. p. 112°). By chlorination in cold glacial acetic acid solution, 4:5-dichloro-2:3-dihydroxytoluene yields a *keto-chloride*, yellow prisms, m. p. 86—89°, which is reduced by stannous chloride to 4:5:6-trichloro-2:3-dihydroxytoluene. By oxidation with nitric acid (D 1·15) 4:5-dichloro-2:3-dihydroxytoluene yields 4:5-*dichloro*-2:3-*toluquinone*, dark red needles, m. p. 83°.

By treatment with nitric acid (D 1·48) 3:5:6-trichloro-*o*-cresol yields 3:5:6-*trichloro-o-cresol-nitroquinitrol*,

$$NO_2\cdot O\cdot C(OH){<}{\substack{CMe(NO_2)\cdot CCl \\ CCl{=\!=\!=}CH}}{>}CCl,$$

unstable, colourless crystals, m. p. 91° (decomp.). This differs from the 3:4:5-trichloro-isomeride in not being convertible into a dichlorotoluquinone nitrate, but resembles it in being converted into the trichlorotoluquinone by concentrated sulphuric acid. By boiling its solution in glacial acetic acid until nitrous fumes cease to be evolved and then reducing the cold solution with stannous chloride, 3:5:6-trichloro-*o*-cresol is regenerated. The nitroquinitrol is reduced by stannous chloride and dilute hydrochloric acid to 5:6-*dichloro-3-amino-o-cresol*, colourless needles (*hydrochloride*, needles; *diacetyl* derivative, needles, m. p. 204—205°), which is converted by chlorination in glacial acetic acid into a keto-chloride yielding 4:5:6-trichloro-2:3-dihydroxytoluene.

3:5-*Dichloro-o-cresol-nitroquinitrol*,

$$NO_2\cdot O\cdot C(OH){<}{\substack{CMe{=\!=\!=}CH \\ CCl(NO_2)\cdot CH}}{>}CCl,$$

colourless needles, m. p. 109° (decomp.), obtained from 3:5-dichloro-*o*-cresol and nitric acid (D 1·48) is more stable than the two preceding nitroquinitrols, but it also decomposes slowly by keeping. It can be converted into 5-*chloro-3-nitro-o-cresol*, yellow needles, m. p. 107° (*acetyl* derivative, colourless needles, m. p. 88°), 5-*chloro-3-amino-o-cresol*, colourless needles, m. p. 107° (*hydrochloride*, leaflets; *diacetyl* derivative, needles, m. p. 196°), 4:5:6-trichloro-2:3-dihydroxytoluene, and 5-*chloro-o-toluquinone* 2-*nitrate*,

$$NO_2\cdot O\cdot C(OH){<}{\substack{CMe{:}CH \\ CO{-}CH}}{>}CCl,$$

yellow crystals, m. p. 117—118°, by the methods described above. The last-mentioned compound is reduced by stannous chloride solution to 5-*chloro*-2:3-*dihydroxytoluene*, colourless needles, m. p. 89° (*diacetyl* derivative, needles, m. p. 65—66°), by stannous chloride

solution and concentrated hydrochloric acid to *5-chloro-6-amino-2:3-dihydroxytoluene*, colourless leaflets, m. p. 150—160° (*hydrochloride*, needles; *triacetyl* derivative, needles, m. p. 183°; *tetraacetyl* derivative, leaflets, m. p. 135°), and by stannous chloride solution at 0° into *5-chloro-6-nitro-2:3-dihydroxytoluene*, yellow needles and prisms, m. p. 135° (*diacetyl* derivative, colourless leaflets, m. p. 148°).

By chlorinating 5-chloro-6-amino-2:3-dihydroxytoluene hydrochloride in suspension in glacial acetic and concentrated hydrochloric acids a yellow keto-chloride is obtained, which by reduction in alcoholic solution with stannous chloride yields *5-chloro-2:3:6-trihydroxytoluene*, colourless needles, m. p. 175°; this forms a *triacetyl* derivative, needles, m. p. 95°, and yields *5-chloro-2-hydroxy-p-toluquinone*, pale red needles, m. p. 160°, by oxidation with nitric acid (D 1·15).

By treatment with nitric acid (D 1·48) at 0°, 4:5-dichloro-*o*-cresol yields *4:5-dichloro-3-nitro-o-cresol-nitroquinitrol*,

$$NO_2\cdot O\cdot C(OH)<\begin{matrix}CMe{=\!=}CH\\C(NO_2)_2\cdot CCl\end{matrix}>CCl,$$

colourless needles, m. p. 110° (decomp.), which yields 4:5-dichloro-*o*-toluquinone 2-nitrate (above) by boiling in tetrachloroethane solution and 4:5-dichloro-3-nitro-*o*-cresol by reduction with stannous chloride in methyl-alcoholic solution at 0°.

4-Chloro- and 6-chloro-*o*-cresols, by treatment with nitric acid, yield, not nitroquinitrols, but *4-chloro-3:5-dinitro-o-cresol*, yellow needles, m. p. 146° (*acetyl* derivative, colourless needles, m. p. 109—110°), and *6-chloro-3:5-dinitro-o-cresol*, yellow needles, m. p. 82—83° (*acetyl* derivative, colourless needles, m. p. 95°), respectively. C. S.

Chlorotrihydroxytoluenes. TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1918, **417**, 236—254).—*3-Chloro-6-nitro-o-cresol*, colourless needles, m. p. 79° (*acetyl* derivative, leaflets, m. p. 84°), prepared by treating 6-nitro-*o*-cresol in chloroform solution with the calculated quantity of chlorine, is converted by nitric acid (D 1·48) at 0° into *3-chloro-5:6-dinitro-o-cresol*, stout, faintly yellow needles or prisms, m. p. 134° (*acetyl* derivative, colourless needles, m. p. 136°), which in alcoholic solution is reduced by stannous chloride solution to *3-chloro-5:6-diamino-o-cresol*, colourless needles (*triacetyl* derivative, colourless needles, m. p. 236°), the *hydrochloride* of which, stout needles, by chlorination in glacial acetic and concentrated hydrochloric acids yields *1:3:3:4:4-pentachloro-2:5:6-triketo-1-methylcyclohexane*, $CMeCl<\begin{matrix}CO\cdot CCl_2\\CO{-}CO\end{matrix}>CCl_2$, yellow plates, m. p. 68°. This keto-chloride is reduced by stannous chloride solution to 3-chloro-2:5:6-trihydroxytoluene, m. p. 175°, which is identical with the substance obtained by Zincke and Preiss from 3:5-dichloro-*o*-cresol-nitroquinitrol (preceding abstract).

By methods similar to the preceding, the following substances

have been prepared, starting with 4-nitro-*o*-cresol; 3-*chloro-4-nitro-o-cresol*, faintly yellow needles or leaflets, m. p. 74° (*acetyl* derivative, colourless needles or leaflets, m. p. 59°); 3-*chloro-4:5-dinitro-o-cresol*, faintly yellow needles, m. p. 139° (*acetyl* derivative, colourless needles, m. p. 167°); 3-*chloro-4:5-diamino-o-cresol*, colourless needles (*hydrochloride*, colourless needles, *triacetyl* derivative, needles, m. p. 230°, *azine* from phenanthraquinone, $C_{21}H_{13}ON_2Cl$, brownish-yellow leaflets, m. p. 273°); 1:3:3:6:6-*pentachloro-2:4:5-triketo-1-methyl*cyclo*hexane*, $C_7H_3O_3Cl_5$, pale yellow plates and prisms, m. p. 78°; and 3:6-*dichloro-2:4:5-trihydroxytoluene*, colourless needles, m. p. 155° (*triacetyl* derivative, needles, m. p. 151°). The last substance is oxidised by nitric acid (D 1·15), followed by acid, D 1·4, to 3:6-*dichloro-4-hydroxy-p-toluquinone*, red needles, m. p. 157°.

An alkaline solution of 3-chloro-4:5-diamino-*o*-cresol is oxidised by air to 3-*chloro-4-amino-p-toluquinone-5-imide*, $C_7H_7ON_2Cl$, red needles, m. p. 175—177° (decomp.; blackening at about 160°), which exhibits basic properties. 3-Chloro-4:5-diamino-*o*-cresol hydrochloride is oxidised by *N*-ferric chloride solution to 3-*chloro-4-amino-p-toluquinone*, dark red needles, m. p. about 142°, which is reduced by stannous chloride to 3-*chloro-4-amino-2:5-dihydroxytoluene*, colourless needles (*hydrochloride*, leaflets; *triacetyl* derivative, needles, m. p. 185°). C. S.

Organic Chemical Reagents. III. β-Phenylhydroxylamine and "Cupferron" (Ammonium Salt of Nitrosophenylhydroxylamine). C. S. Marvel and Oliver Kamm (*J. Amer. Chem. Soc.*, 1919, **41**, 276—282. Compare A., 1918, i, 482; this vol., i, 61).—The statement made by various authors that β-phenylhydroxylamine is obtainable in theoretical yield by the reduction of nitrobenzene by means of zinc dust is inaccurate. Directions are now given for the reduction of nitrobenzene in portions of 500 grams, a yield of the dry product amounting to 64% of the theoretical being obtainable.

For the preparation of "cupferron," dry β-phenylhydroxylamine is not required, and the conditions are given under which the moist product is treated in ethereal solution with ammonia and amyl nitrite so as to obtain "cupferron" in a yield 80—90% of that theoretically possible. Even with the present high prices of materials and labour, "cupferron" may be made in the laboratory, where the labour charge is an abnormally high proportion of the total expenses, at a cost considerably less than the pre-war price of the product. [See *J. Soc. Chem. Ind.*, 1919, April.] T. H. P.

The Identification of Acids. IV. Phenacyl Esters. J. B. Rather and E. Emmet Reid (*J. Amer. Chem. Soc.*, 1919, **41**, 75—83).—In previous communications (A., 1917, i, 334, 559) the use of *p*-nitrobenzyl bromide for the identification of organic acids by the melting points of their *p*-nitrobenzyl esters was described. It is now shown that phenacyl bromide (ω-bromoacetophenone) may

be employed in a precisely similar manner and that in some cases the phenacyl esters of the acid are still more definitely characteristic than the *p*-nitrobenzyl esters. Phenacyl bromide is prepared by bromination of acetophenone in glacial acetic acid solution. The acid is neutralised with rather less than the theoretical quantity of sodium carbonate, and, working with 0·05 gram-mol. of the reagents, this quantity is dissolved in 5 c.c. of water, 1 gram of phenacyl bromide is added and then 10 c.c. of 95 per cent. alcohol. The ester is obtained after boiling for one hour with monobasic, two hours with dibasic, and three hours with tribasic acids. It is recrystallised from dilute alcohol until the melting point is constant. The following phenacyl esters have been characterised: acetate, m. p. 40°; *aconitate*, m. p. 90°; *o-aminobenzoate*, m. p. 181—182°; benzoate, m. p. 118·5°; p-*bromobenzoate*, m. p. 87°; *cinnamate*, m. p. 140·5°; *citraconate*, m. p. 108·5°; *citrate*, m. p. 104°; m-*cresotate*, m. p. 116·5°; *o-cresotate*, m. p. 138·5°; p-*cresotate*, m. p. 145·5°; *fumarate*, m. p. 197·5°; *glutarate*, m. p. 104·5°; *itaconate*, m. p. 79·5°; *lactate*, m. p. 96°; *malate*, m. p. 106°; *maleate*, m. p. 119°; p-*nitrobenzoate*, m. p. 128·4°; *palmitate*, m. p. 52·5°; *pyrotartrate*, m. p. 101·5°; *saccharate*, m. p. 120°; *salicylate*, m. p. 110°; *stearate*, m. p. 64°; *succinate*, m. p. 148°; *tartrate*, m. p. 130°. J. F. B.

Pschorr's Phenanthrene Synthesis. II. Fritz Mayer and Frank Albert English (*Annalen*, 1918, **417**, 60—92. Compare Mayer and Balle, A., 1914, i, 536).—As the result of the experiments here recorded, it appears impossible to synthesise 8-, 5-, or 7-ethylphenanthrene by any of the methods at present known.

o-*Ethylbenzyl alcohol*, $C_6H_4Et\cdot CH_2\cdot OH$, b. p. 229°, obtained by the electrolytic reduction of *o*-ethylbenzoic acid at a lead cathode in dilute sulphuric acid solution, is converted by cold saturated hydrobromic acid into o-*ethylbenzyl bromide*, colourless crystals, m. p. 34°, b. p. 225°/751 mm. The latter is converted by alcoholic sodium cyanide into *o-ethylphenylacetonitrile*, $C_6H_4Et\cdot CH_2\cdot CN$, b. p. 257—258°/752 mm., which is hydrolysed by heating with 35% potassium hydroxide solution (2 mols.) and 30% hydrogen peroxide (3 mols.), yielding *o-ethylphenylacetic acid*, m. p. 83·5° (*ethyl* ester, a colourless, odourless oil). Attempts to reduce this acid to o-*ethylbenzaldehyde*, a colourless, odourless liquid, b. p. 210°/753 mm., by the methods of Mettler and Piria gave unsuccessful or unsatisfactory results, but the aldehyde is obtained in 67% yield by oxidising *o*-ethylbenzyl alcohol with potassium dichromate and 10% sulphuric acid, and in 33·6% yield by heating *o*-ethylbenzyl bromide with hexamethylenetetramine in 60% alcoholic solution. Further experiments were undertaken to ascertain the influence of negative substituents in the benzene nucleus on the Sommelet reaction. *o*-Nitrobenzyl chloride and hexamethylenetetramine, boiled in 60% alcoholic solution for four hours, yielded, in addition to a small quantity of a *substance*, $C_{23}H_{15}O_7N_5$, m. p. 153·5°, a substance, m. p. 112°, which is regarded as *tri-o-nitro-*

benzyltrimethylenetriamine, $NX<\substack{CH_2\cdot NX \\ CH_2\cdot NX}>CH_2$ [where X is $NO_2\cdot C_6H_4\cdot CH_2$], since its molecular weight corresponds with this formula, and it yields formaldehyde and *o*-nitrobenzylamine hydrochloride by hydrolysis with boiling concentrated hydrochloric acid. In a similar manner, *p*-nitrobenzyl chloride and hexamethylenetetramine yield *tri*-p-*nitrobenzyltrimethylenetriamine*, m. p. 161°, whilst *o*- and *p*-chlorobenzyl chlorides yield *o*- and *p*-chlorobenzaldehydes respectively.

The attempt to condense *o*-ethylbenzaldehyde and sodium *o*-nitrophenylacetate by means of acetic anhydride and zinc chloride at 120° in an atmosphere of carbon dioxide yielded a very small quantity of a *substance*, $C_9H_9O_3N$, colourless crystals, m. p. 183·5°. A similar attempt to condense *o*-nitrobenzaldehyde and potassium *o*-ethylphenylacetate for two days at 100° yielded *β-o-nitrophenyl-α-o-ethylphenylacrylic acid*,

$$NO_2\cdot C_6H_4\cdot CH\colon C(C_6H_4Et)\cdot CO_2H,$$

m. p. 194°. By reduction with ferrous sulphate and aqueous ammonia, it yields the corresponding *amino*-acid, colourless crystals, m. p. 178—179°, but the attempt to convert this into 8-ethylphenanthrenecarboxylic acid by shaking its diazotised solution with copper powder or by boiling with water yielded in the first case a non-crystallisable product, and in the second case *β-o-hydroxyphenyl-α-o-ethylphenylacrylic acid*, $C_{17}H_{16}O_3$, m. p. 205°.

The starting material in the attempt to synthesise 5- or 7-ethylphenanthrene is acetophenone, which by successive nitration and reduction yields *m*-aminoacetophenone. The latter is converted by hydrazine hydrate at 160° into a mixture of the *azine*, $C_{16}H_{18}N_4$, m. p. 147°, and the *hydrazone*, $C_8H_{11}N_3$, m. p. 98°, which is reduced by Wolff's sodium ethoxide method at 160° to *m*-ethylaniline; Staudinger and Kupfer's method of reduction with hydrazine hydrate at 210°, however, gives a greatly improved yield. *m*-Ethylaniline is converted by Sandmeyer's method into m-*ethylbenzonitrile*, $C_6H_4Et\cdot CN$, b. p. 116—117°/25 mm. This is hydrolysed to *m*-ethylbenzoic acid, from which, by methods similar to those used in the ortho-series above, are obtained in succession m-*ethylbenzyl alcohol*, b. p. 227°/758 mm., m-*ethylbenzyl bromide*, m-*ethylphenylacetonitrile*, $C_6H_4Et\cdot CH_2\cdot CN$, b. p. 250—254°/761 mm., m-*ethylphenylacetic acid*, m. p. 62—64°, and m-*ethylbenzaldehyde*, b. p. 212°.

Potassium *m*-ethylphenylacetate and *o*-nitrobenzaldehyde, condensed together by means of zinc chloride and acetic anhydride at 120° in an atmosphere of carbon dioxide, yield *β-o-nitrophenyl-α-m-ethylphenylacrylic acid*, m. p. 138°. This is reduced by ferrous sulphate and ammonia to the *amino*-acid, $C_{17}H_{17}O_2N$, m. p. 150—150·5°, the diazotised solution of which yields by boiling or by shaking with copper powder a mixture of *β-o-hydroxyphenyl-α-m-ethylphenylacrylic acid*, m. p. 203° (decomp.), and an *ethylphenanthrenecarboxylic acid*, $C_{17}H_{14}O_2$, m. p. 147—149°, which is

probably 5-ethylphenanthrene-9-carboxylic acid. Attempts to convert the latter into ethylphenanthrene by heating under ordinary or reduced pressure were unsuccessful. C. S.

Hydroxy-carbonyl Compounds. I. New Synthesis of Hydroxy-aldehydes. P. KARRER (*Helv. Chim. Acta*, 1919, **2**, 89—94).—A rapid current of hydrogen chloride is passed for several hours into dry ether containing resorcinol, cyanogen bromide, and anhydrous zinc chloride. The crystals of the intermediate product, which contains chlorine, but not bromine, are collected and dissolved in cold water, and the solution, after being washed with ether, is boiled for twenty minutes. The 2:4-dihydroxybenzaldehyde, which is thus produced in good yield, is extracted with ether. It appears to be formed by the reactions: (i) $CBrN + HCl = CHBr{:}NCl$; (ii) $CHBr{:}NCl + C_6H_4(OH)_2 = C_6H_3(OH)_2{\cdot}CH{:}NCl + HBr$; (iii) $C_6H_3(OH)_2{\cdot}CH{:}NCl \xrightarrow{H_2O} C_6H_3(OH)_2{\cdot}CHO$.

Phloroglucinol reacts in a similar manner. C. S.

Phenols Insoluble in Alkali Hydroxides. ROGER ADAMS (*J. Amer. Chem. Soc.*, 1919, **41**, 247—270).—Investigation has been made of the phenylhydrazones of the *o*-hydroxyaldehydes and ketones in order to determine the structure characteristic of such compounds of this type as are insoluble in alkali hydroxides. The results show that the introduction of a methyl group, or, in general, of a group containing carbon, into either the phenolic ring or the side-chain of one of these phenylhydrazones is accompanied by marked depression of the solubility of the compound in 10% aqueous sodium hydroxide. A bromine atom produces a less effect, which is the more noticeable with substitution in the side-chain. When a nitro-group is introduced into the phenolic ring in the ortho- or para-position to the hydroxyl group, the solubility in alkali is increased, and a nitro-group in the para-position in the phenylhydrazone residue has the same effect. This result is regarded as due to the possibility of the rearrangement of nitrophenols and of *p*-nitrophenylhydrazones to aci-nitro-compounds, which are readily soluble in alkali. Where there is no tendency to form aci-nitro-compounds, as with the *m*- and *o*-nitrophenylhydrazones, the nitro-group has the same effect as other groups and increases the insolubility in alkali hydroxides. No compound with a nitro-group in the meta-position to the hydroxyl was prepared, but such a compound should show diminished solubility in alkali. Comparison of the phenylhydrazones of *p*-homosalicylaldehyde and pæonol with the corresponding hydrazones, the former being insoluble and the latter soluble in alkali hydroxides, shows that a large group like phenyl in the hydrazone residue is absolutely necessary for the compound to show insolubility in alkali. The marked effect of a methyl or phenyl group attached to the carbon atom carrying the phenylhydrazone residue, as compared with a hydrogen atom, is shown by the perfect solubility of the azines of *p*-homosalicyl-

aldehyde and β-naphthaldehyde in cold alkali hydroxide solution and the insolubility of the azines of pæonol and 2-hydroxy-5-methylbenzophenone in boiling alkali. Finally, a substituent group attached to the iminic nitrogen has a decided effect in reducing the solubility in alkali hydroxides.

The various explanations which have been advanced to account for the insolubility of these phenolic compounds in alkali hydroxide solution are discussed and shown to be unsatisfactory, and the author regards this behaviour as due to the fact that such compounds are very weak acids and highly insoluble in water. Any insoluble, slightly hydrolysed acid would be expected to behave similarly, and the introduction into its molecule of a positive or negative atom or group will have a result determined by two distinct effects: first, the insolubility in water due to the increased size of the whole molecule, this leading to increased insolubility in alkali hydroxide, and, secondly, an increase or a decrease in the acidity of the whole molecule, depending on the nature and position of the group introduced.

Pæonol phenylhydrazone is soluble in hot alkali solution; the *hydrazone*, $C_9H_{12}O_2N_2$, white plates, quickly turning yellow on exposure, m. p. 73—75°, dissolves in cold alkali hydroxide; the *azine*, $C_{18}H_{20}O_4N_2$, lemon-yellow crystals, m. p. 226—227°, is insoluble in boiling alkali hydroxide; the 2:4:6-*tribromophenylhydrazone*, $C_{15}H_{12}O_2N_2Br_3$, white needles, m. p. 162°, is insoluble in boiling alkali hydroxide.

Bromopæonol, $C_9H_9O_3Br$, has m. p. 169° (Brüll and Friedländer, A., 1897, i, 221, gave 171°); its *phenylhydrazone*, $C_{15}H_{15}O_2N_2Br$, slender, yellow needles, m. p. 172·5—173·5°, its p-*bromophenylhydrazone*, dull yellow, monoclinic plates, m. p. 189·5°, and its 2:4:6-*tribromophenylhydrazone*, white needles, m. p. 169—171°, are insoluble in boiling alkali hydroxide. Its *methyl* ether, $C_{10}H_{11}O_3Br$, forms white needles, m. p. 139—140°; neither this methyl ether nor that of pæonol itself yields a phenylhydrazone in the ordinary way.

ω-*Tribromobromopaeonol*, $OH{\cdot}C_6H_2Br(OMe){\cdot}CO{\cdot}CBr_3$, forms lemon-yellow needles, m. p. 123—124°. *Bromonitropaeonol*,

$$C_9H_8O_5NBr,$$

forms long, hairy needles, m. p. 112—114°; its *phenylhydrazone*, $C_{15}H_{14}O_4N_3Br$, forms saffron-coloured crystals, m. p. 204·5—205·5°, and dissolves gradually in cold, readily in warm alkali. *Nitropaeonol*, $C_9H_9O_5N$, forms white needles, m. p, 155°; its *phenylhydrazone*, $C_{15}H_{15}O_4N_3$, orange needles, m. p. 215·5—216·5°, is soluble slightly in cold, readily in warm alkali hydroxide; its *methyl ether*, $C_{10}H_{11}O_5N$, forms slender, white needles, m. p. 131°, gradually turning yellowish-red. *Aminopaeonol*, $C_9H_{11}O_3N$, forms greenish-yellow, monoclinic prisms, m. p. 112—113°; its *platinichloride* was prepared and analysed.

Dinitroacetylresacetophenone, $C_6HAc(OH)(OAc)(NO_2)_2$, forms white plates, m. p. 121—122°. *Dinitroresacetophenone*,

$$C_6HAc(OH)_2(NO_2)_2,$$

forms pale yellow crystals resembling fine sand, m. p. 166—167°, and its *phenylhydrazone*, $C_{14}H_{12}O_6N_4$, reddish-brown crystals darkening at 238° and decomposing at 242·5°. *Acetylaminoresacetophenone*, $C_6H_2Ac(OH)_2\cdot NHAc$, forms white needles, m. p. 254°. *Nitroresodiacetophenone*, $C_6HAc_2(OH)_2\cdot NO_2$, forms white needles, m. p. 231°; its *phenylhydrazone*, $C_{16}H_{15}O_5N_3$, pale yellow powder, darkening at 220° and decomposing sharply at 235°, is soluble in cold alkali hydroxide; its *diphenylhydrazone*,

$$NO_2\cdot C_6H(OH)_2(CMe:N_2HPh)_2,$$

massive, lemon-yellow needles, becoming orange-red and decomposing at 273°, dissolves slightly in cold and readily in warm alkali hydroxide.

Bromoresodiacetophenone, $C_{10}H_9O_4Br$, forms white plates, m. p. 205°.

Salicylaldehyde *o*-tolylhydrazone dissolves in alkali hydroxide only in the hot; the 2:4:6-*tribromophenylhydrazone*, white needles, m. p. 100°, dissolves gradually, with decomposition, in boiling alkali hydroxide.

Di-5-nitrosalicylidenebenzidine,

$$[C_6H_3(OH)(NO_2)\cdot CH]_2N_2(C_6H_4)_2,$$

forms red crystals not melting below 275° and dissolves partly in boiling alkali hydroxide. *Di-3-nitrosalicylidenebenzidine* forms bright red crystals not melting below 275°, and is somewhat more soluble in boiling alkali hydroxide than the 5-isomeride.

p-Homosalicylaldehydephenylhydrazone is soluble in hot alkali hydroxide; the *hydrazone*, $C_8H_{10}ON_2$, white powder, m. p. 72—74°, dissolves in cold alkali hydroxide.

Bromo-p-homosalicylaldehyde, $C_8H_7O_2Br$, forms yellow crystals shrinking at 63°, m. p. 65°, and its *phenylhydrazone*, $C_{14}H_{13}ON_2Br$, dirty yellow crystals, m. p. 140—141°, soluble in hot alkali hydroxide.

5-*Methyl-2-hydroxybenzophenoneazine*, $[C_6H_3Me(OH)\cdot CPh]_2N_2$, forms lemon-yellow crystals, m. p. 259—260°, and is insoluble in boiling sodium hydroxide solution. T. H. P.

Pinacolin Transformations. IV. Ring Changes produced by the Elimination of Water from Alicyclic Alcohols. HANS MEERWEIN (*Annalen*, 1918, **417**, 255—277. Compare A., 1914, i, 850).—In connexion with the previous investigation (*loc. cit.*), 1-methyl-1-α-hydroxyethyl*cyclo*pentane has been synthesised and also submitted to the dehydrating action of zinc chloride, and the constitution of the resulting hydrocarbon has been determined; it is 1:2-dimethyl-Δ^1-*cyclo*hexene, and the reaction is one of the smoothest changes known of a *cyclo*pentane into a *cyclo*hexane derivative.

[With CL. FLEISCHHAUER.]—The reaction between magnesium and 1-chloro-1-methyl*cyclo*pentane in ether at 5—10°, preferably in the absence of air, and treatment of the product with carbon dioxide and subsequently with ice-water and dilute sulphuric acid, lead to the formation of 1-methyl*cyclo*pentane-1-carboxylic acid,

the acid chloride of which reacts with magnesium methyl iodide in ether at $-15°$ to form, after the usual treatment, 1-*methyl*-1-cyclo*pentyl methyl ketone*, $C_5H_8Me{\cdot}COMe$, b. p. 48·4°/10 mm., in good yield, the *semicarbazone* of which forms colourless needles, m. p. 143—144°. By reduction with sodium and moist ether, the ketone yields 1-*methyl*-1-α-*hydroxyethyl*cyclo*pentane*, $C_5H_8Me{\cdot}CHMe{\cdot}OH$, b. p. 67·6°/10·5 mm., together with the corresponding *pinacone*, $C_{16}H_{30}O_2$, colourless prisms, m. p. 89—90°, the former of which yields only 1:2-dimethyl-Δ^1-*cyclo*hexene by heating with zinc chloride at 180—190°.

The acid chloride of 1:2:2:3-tetramethyl*cyclo*pentane-1-carboxylic acid reacts with zinc methyl or, better, magnesium methyl iodide in ether to form, ultimately, 1:2:2:3-*tetramethyl*-1-cyclo*pentyl methyl ketone*, $C_{11}H_{20}O$, b. p. 101—102°/18 mm. (*semicarbazone*, m. p. 232°), which is reduced by sodium and moist ether to 1:2:2:3-*tetramethyl*-1-α-*hydroxyethyl*cyclo*pentane*, $C_{11}H_{22}O$, b. p. 108—109°/15 mm. The alcohol appears to be a mixture of two stereoisomeric forms, since it partly solidifies, the solid form having m. p. 70—71°, $D_4^{40\cdot2}$ 0·9113 (supercooled), $n_D^{40\cdot2}$ 1·46322. By heating with zinc chloride, the alcohol yields a mixture of 1:2:3:3:4-pentamethyl-Δ^1-*cyclo*hexene (chief product) and 1:2:2-trimethyl-3-*iso*propyl-Δ^3-*cyclo*pentene, the constitutions of which are deduced from the nature of the products of the decomposition of the ozonides. C. S.

*meso*Naphthadianthrones. ALFRED ECKERT and RUDOLF TOMASCHEK (*Monatsh.*, 1918, **39**, 839—864).—The authors have endeavoured to synthesise derivatives of *meso*naphthadianthrone in a manner which leaves no doubt as to their constitution. For this purpose the method of Scholl, Mansfield, and Potschiwauscheg (A., 1910, i, 494) as modified by Ullmann and Minajeff (A., 1912, i, 366) has been applied to certain αα′-dichloroanthraquinones; of these only the 1:4-derivative reacts with copper powder, the 1:5- and 1:8-dichloro- and the 1:4:5:8-tetrachloro-products remaining unattacked. The procedure of Meyer, Bondy, and Eckert (A., 1913, i, 62) is not applicable to halogenated anthraquinones, since the halogen is partly eliminated during reduction with zinc and alkali. A more successful process consists in converting the anthranols into the corresponding dihydrodianthrones, enolisation of the latter (enolisation by alkali occurs less readily with derivatives than with the parent substance and the products are considerably less stable), and oxidation of the material so formed to the dianthrone; the latter is converted into the corresponding *meso*naphthadianthrone when exposed to light. In cases in which formation of the *meso*-naphthalene ring cannot occur by simple elimination of hydrogen, a peculiar phenomenon is observed; when dissolved in nitrobenzene or xylene, the substance is unchanged after protracted illumination, whilst in concentrated sulphuric acid solution elimination of two atoms of hydrogen and two of chlorine slowly occurs.

4 : 4′-*Dichloro*-1 : 1′-*dianthraquinonyl*,

$$C_6H_4{<}{CO \atop CO}{>}C_6H_3Cl\cdot C_6H_3Cl{<}{CO \atop CO}{>}C_6H_4$$

pale yellow crystals, is reduced by copper powder and concentrated sulphuric acid to 4 : 4′-*dichloro*meso*benzdianthrone*, yellowish-brown needles, which under the action of light pass into 4 : 4′-*dichloro*meso*naphthadianthrone*, $CO{<}{C_6H_2Cl \atop C_6H_3}{>}C{=}C{<}{C_6H_2Cl \atop C_6H_3}{>}CO$, small, yellow needles.

1(or 4)-*Chloroanthrone*, yellow needles, m. p. 106°, obtained by the reduction of 1-chloroanthraquinone by aluminium bronze and sulphuric acid, is oxidised by ferric chloride to 4 : 4′-*dichlorodihydrodianthrone*, colourless crystals which darken without melting at 270°. The enolic *form* of this substance is an unstable, green powder, which is readily converted by persulphate into 4 : 4′-*dichlorodianthrone*, greenish-yellow crystals, from which 4 : 4′-dichloro-*meso*naphthadianthrone is obtained by exposure to light.

1 : 4-*Dichloroanthrone*, yellow needles, m. p. 136—138°, 1 : 4 : 1′ : 4′-*tetrachlorodihydrodianthrone*, colourless crystals, m. p. 250° (decomp.), and 1 : 4 : 1′ : 4′-*tetrachlorodianthrone*, yellow plates, are prepared by a similar series of reactions; the latter substance loses two atoms of hydrogen and two of chlorine when its solution in concentrated sulphuric acid is exposed to light, but the product obtained did not give sharp analytical results.

1 : 5-Dichloroanthrone yields 1 : 5 : 1′ : 5′-*tetrachlorodihydrodianthrone*, colourless crystals, and 1 : 5 : 1′ : 5′(or 4 : 8′)-*tetrachlorodianthrone*, yellow platelets; the corresponding *meso*naphthadianthrone could not be obtained in the pure state. Similarly, 1 : 8-*dichloroanthrone*, yellow needles, m. p. 115°, 4 : 5 : 4′ : 5′-*tetrachlorodihydrodianthrone*, colourless crystals which remain unchanged up to 280°, 4 : 5 : 4′ : 5′-*tetrachlorodianthrone*, pale yellow crystals, and 4 : 5 : 4′ : 5′-tetrachloro*meso*naphthadianthrone, small, yellow needles, were prepared.

3 : 3′-*Dibromo*meso*benzdianthrone* forms a reddish-yellow, crystalline powder which is converted by light into 3 : 3′-*dibromo*meso*naphthadianthrone*, pale yellow powder.

Starting from 1 : 3-dichloroanthraquinone (Meyer and Zahn, A., 1913, i, 455), the constitution of which is now definitely established by its conversion into 1 : 3-diphenoxyanthraquinone (Ullmann and Eiser, A., 1916, i, 823), the following series of substances is obtained: 3 : 3′-*dichloro*-1 : 1′-*dianthraquinonyl*, greenish-yellow needles, 3 : 3′-*dichloro*meso*benzdianthrone*, yellowish-brown needles, and 3 : 3′-*dichloro*meso*naphthadianthrone*, small, yellow needles. Attempts to prepare the substance last named from 2-chloroanthraquinone led to a different product through the following stages: 2-*chloroanthrone*, yellow needles, m. p. 115—120°, which are readily oxidised; 3 : 3′(3 : 2′)-*dichlorodihydrodianthrone*, silvery, crystalline powder, m. p. 240° (decomp.); 3 : 3′(3 : 2′)-*dichlorodianthranol*, greenish-yellow, crystalline powder; *dichlorodianthrone*, yellow,

crystalline powder, in which the position of the chlorine atoms is not decided; and (3:6′)-*dichloromesonaphthadianthrone*, small, yellow needles. H. W.

Constitutions of the Fenchene Hydrocarbons. WALTER QVIST (*Annalen*, 1918, **417**, 278—324).—The author has examined the fenchenes obtained by different methods and having b. p.'s below 150°. He shows that Aschan was right in stating that β-pinolene (*cyclo*fenchene) occurs in the fenchene fraction, b. p. below 150°, obtained from fenchyl chloride. Kondakov and Lutschinin's hydrocarbon (A., 1907, i, 713) is not β-pinolene, but is identical with the author's *iso*fenchylene.

When *Dl*-fenchyl alcohol is heated with aluminium phosphate at 210° or with potassium hydrogen sulphate at 200°, the hydrocarbons obtained contained *d*-β-fenchene and a little *l*-α-fenchene in the fraction of high b. p. (152—155°) and *d*-*cyclo*fenchene and *i*-*iso*fenchylene in the fractions, b. p. 141—143° and 143—145°. *d*-*cyclo*Fenchene is also obtained by heating *Dl*-fenchyl xanthate at 230°, *l*-α-fenchene also being produced. Since both these hydrocarbons yield the same hydrochloride, which yields *l*-α-fenchene by heating with *o*-toluidine, the xanthate method is an excellent means of preparing pure *l*-α-fenchene.

Very pure *d*-β-fenchene (*dibromide*, $C_{10}H_{16}Br_2$, crystals, m. p. 81—82°, $[\alpha]_D^{24.5}$ −31·2° in ethyl acetate) is obtained by heating *l*-*iso*fenchyl chloride with *o*-toluidine. By the xanthate method *l*-*iso*fenchyl alcohol yields *l*-*iso*fenchylene.

β-Pinolene yields two dibromides, namely, *l*- and *i*-α-fenchene dibromides. This proves that Aschan's β-pinolene and the author's tricyclic hydrocarbon obtained from *Dl*-fenchyl alcohol are identical, with the difference, however, that the latter is feebly dextrorotatory *d*-*cyclo*fenchene whilst the former is a mixture of *l*-*cyclo*fenchene and *dl*-*cyclo*fenchene.

The reduction of *d*-α-fenchene dibromide by zinc dust and 75% alcohol at 55° yields fenchane and *l*-α-fenchene. As these two hydrocarbons contain different skeletons, no conclusions can be drawn as to the constitution of the α-fenchene dibromide. C. S.

Phenylurethanes of Terpene Alcohols and Phenols. F. WEEHUIZEN (*Pharm. Weekblad*, 1919, **56**, 299—301).—The terpene alcohol or phenol is dissolved in petroleum (distilling between 170° and 200°). The requisite quantity of phenylcarbimide is added and the solution boiled. On cooling, the phenylurethane crystallises out in quantitative yield and is recrystallised from benzene (80—100°). The phenylurethanes of the following substances were prepared: *o*-, *m*-, *p*-cresol (m. p. 141°, 121—122°, 111—112° respectively), thymol (m. p. 106—107°), menthol (m. p. 111—112°), borneol (m. p. 137—138°), eugenol (m. p. 95°).

The method may be used for the separation of camphor and borneol. The former is unacted on and remains in solution; the latter separates out as bornylphenylurethane. W. S. M.

Constituents of Resins. IV. β-Dammar-resin. Alois Zinke and Erna Unterkreuter (*Monatsh.*, 1918, **39**, 865—869).—Analyses and determinations of molecular weight show the hydrocarbon portion of β-dammar-resin (compare Dulk, *Jahrb. pr. Chem.*, 1848, **45**, 16; Tschirch and Glimmann, A., 1896, i, 164) to have the composition $C_{30}H_{48}$; it melts indefinitely at 195° after softening from 165°, and possibly represents a mixture of hydrocarbons. Attempts have been made to prepare derivatives of it by oxidation, action of nitrous acid, and action of ethereal hydrogen chloride, but definite products have not been isolated. H. W.

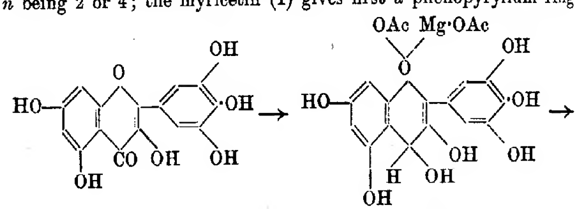
Biochemical Synthesis, by means of Emulsin, of α-Naphthylcarbinyl-β-glucoside. Em. Bourquelot and M. Bridel (*Compt. rend.*, 1919, **168**, 323—324).—When emulsin acts on an acetone solution of dextrose and α-naphthylcarbinol, *α-naphthylcarbinyl-β-glucoside*, long needles, m. p. 156—157° (corr.), $[\alpha]_D$ −71·02°, is obtained, which is readily hydrolysed by emulsin or by dilute sulphuric acid. W. G.

Anthocyanins: Colour Variation in Anthocyanins. Keita Shibata, Yuji Shibata, and Itizo Kasiwagi (*J. Amer. Chem. Soc.*, 1919, **41**, 208—220).—For the reduction of compounds of the flavone and flavanol series, organic acids may be used in conjunction with zinc or magnesium in place of inorganic acids. With monobasic acids deep green to bluish-green pigments are mostly obtained, the tints varying slightly according to the reagents employed. Some of these pigments were isolated and their properties examined.

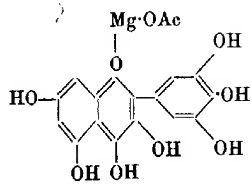
When reduced with magnesium and glacial acetic acid, myricetin gives green compounds of the composition

$$C_{15}H_{11}O_8{\cdot}Mg{\cdot}OAc,[Mg(OAc)_2]_n,$$

n being 2 or 4; the myricetin (I) gives first a phenopyrylium ring



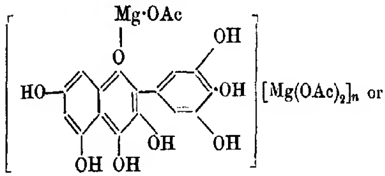
(I.) (II.)

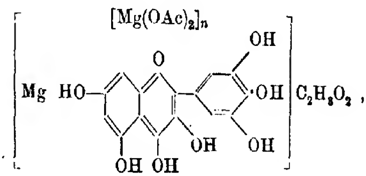


(III.)

(II), the organo-metallic compound (III) then resulting by elimination of acetic acid from the ring.

As the acetates of the bivalent metals often tend to form complex compounds, it was to be expected that addition of magnesium acetate would take place, giving:





according to Werner's co-ordination theory.

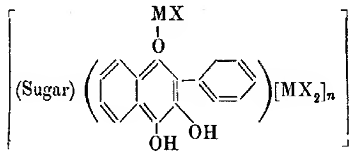
Similarly, myricitrin, a rhamnoside of myricetin, gives with the same reagents a deep blue product co-ordinated with four molecules of magnesium acetate.

The above green or blue pigments are soluble in water as well as in alcohol, giving neutral solutions with the same colours, but the addition of dilute acid (hydrochloric) to the solutions changes the colour to red, the ·Mg·OAc group of the green pigment (III) being replaced by a chlorine atom in the red oxonium salt. This explains why Willstätter and others have always obtained red pigments by reduction of the yellow pigments. Even with inorganic acids green or blue pigments are formed under certain conditions, treatment of myricetin with alcoholic hydrochloric acid yielding a deep green pigment in the molecule of which the position of the Mg·OAc group (III) is occupied by ·MgCl; here addition of magnesium chloride does not take place, probably because of its smaller tendency to form complex salts. The compound dissolves in water and alcohol, giving neutral solutions of the original colour.

That all the above compounds have deep colours or, in other words, that their absorption bands are displaced far towards the red end of the spectrum, is attributed on the one hand to the fact that the phenylpyrylium ring of the green or blue pigments has one more hydroxyl group than that of the oxonium salts, and on the other to the fact that magnesium forms the complexes with its auxiliary valence, which together play the rôle of bathochromism. In the case of the reduced glucoside, flavanol, one of the hydroxyl groups is replaced by a sugar molecule, which shifts the absorption

band hypsochromatically, that is, towards the violet end of the spectrum.

From these results and those of experiments on the pigments of many flowers, the following explanation of the various flower colours is based. The metal organic or complex compounds of reduced flavanol glucosides (annexed formula) are the most important factor in the production of flower colours. The "blue" anthocyanins are the complex compounds of reduced flavanol glucosides, which possess several hydroxyl groups belonging to the flavanol nucleus besides those of sugar molecules, and the metal with which they are



co-ordinated is probably calcium or magnesium, as salts of these metals are always present in the plant cells. The "violet," "violescent red," or "red" pigments are either the analogous metallic complex compounds of flavanol glucosides, which contain fewer of the auxochrome hydroxyl groups, or a mixture of the blue pigments and their products of decomposition by excess of acids, that is, Willstätter's red oxonium salts.

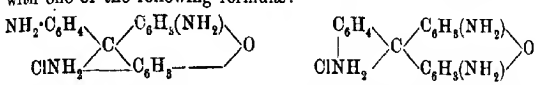
This theory is confirmed by the behaviour of the natural anthocyanin solutions towards the salts of alkaline earth and heavy metals, addition of the latter to alcoholic extracts of various flowers always acting bathochromatically.

Experimental details are given. T. H. P.

A New Yellow Dye and Light Filters made from It. C. E. K. Mees and H. T. Clarke (*Brit. J. Photo.*, 1919, **66**, 48).—The new dye is the *glucosazone* formed by the condensation of dextrose with *p*-hydrazinobenzoic acid; it gives a very soluble *sodium* salt. W. G.

Composition of Pyrocresoles and their Relationship to Coal Tar Constituents. Friedrich Ruszig (*Zeitsch. angew. Chem.*, 1919, **32**, [i], 37—40).—The so-called isomeric pyrocresoles, isolated by Schwarz (A., 1883, 204; 1884, 79) from the residue of the distillation of crude phenol, have the same composition, $C_{15}H_{14}O$, and properties as the compounds prepared by Gladstone and Tribe (T., 1889, **55**, 51) by the decomposition of the aluminium *o*-, *m*-, and *p*-tolyloxides. They have been identified as dimethylxanthen, whilst the homologous compound, $C_{13}H_{10}O$, is xanthen, produced by the decomposition of aluminium phenoxide in accordance with the equation $2Al(O\cdot C_6H_5)_3 = (C_6H_5)_2O + C_{13}H_{10}O + C_6H_5\cdot OH + CH_4 + C_4 + Al_2O_3$. From aluminium *m*-tolyloxide, two isomeric dimethylxanthens, corresponding with Schwarz's *α*- and *β*-pyrocresoles, were prepared, but the third isomeric modification was not found.

Aluminium *p*-tolyloxide yielded symmetrical *p*-dimethylxanthen (m. p. 168°), whilst from aluminium *o*-tolyloxide the 4:5-dimethylxanthen was obtained. The liquids of high boiling point which separate at the end of the distillation of aluminium phenoxide have the composition $C_{19}H_{14}O$, and appear to be formed from xanthen, as follows: $C_{13}H_{10}O + C_6H_5{\cdot}OH = C_{19}H_{14}O + H_2O$. On dissolving this compound in nitric acid and adding water, an amorphous, yellow compound is precipitated. By reducing this with zinc and acetic acid, and precipitating the base with ammonia, a brown colouring matter is obtained. Its hydrochloride is soluble in water and acts as a direct brown dye for wool and silk. This dye, for which the name xanthen-brown is suggested, is an inner ester of magenta and has a constitution corresponding with one of the following formulæ:



Analogous compounds obtained in the distillation of aluminium tolyloxides had the composition of tolyldimethylxanthens and also yielded xanthen-browns, and similar compounds were obtained from the anthracene oils of coal tar, which probably consist, in part, of triphenylmethane derivatives, and, in particular, of phenyl- and diphenyl-xanthens. [See also *J. Soc. Chem. Ind.*, 1919, April.]

C. A. M.

Synthesis of Aminoflavones, of Flavone-azo-β-naphthol Dyes and of other Flavone Derivatives. MARSTON TAYLOR BOGERT and JOSEPH K. MARCUS (*J. Amer. Chem. Soc.*, 1919, **41**, 83—107).—Flavone was prepared by a modification of Ruhemann's method (A., 1913, i, 891), using smaller quantities of aluminium chloride and benzene. Nitration in the cold by nitric and sulphuric acids in glacial acetic acid solution yielded mixtures which were separated into two fractions, consisting of 2′- and 3′-nitroflavones and of 3′- and 4′-nitroflavones. These were converted by reduction with stannous chloride into the aminoflavones, the three isomerides being separated and purified by taking advantage of their different basicities and solubilities. *2′-Aminoflavone* crystallises from hot acetone in silky, pale yellow needles, m. p. 149·5—150·5° (corr.); *3′-aminoflavone* crystallises from pyridine or xylene in lemon-yellow, straight needles, m. p. 156—157° (corr.), and *4′-aminoflavone* crystallises from the same solvents in long, golden-yellow needles, m. p. 234—236° (corr.). From the three aminoflavones, the corresponding hydroxyflavones were prepared by means of the diazonium salts, and were decomposed by sodium ethoxide and alcohol into *o*-hydroxyacetophenone and *o*-, *m*-, and *p*-hydroxybenzoic acids, owing to the rupture of the pyrone ring at the double bond. *2′-Hydroxyflavone* forms lustrous, colourless plates, m. p. 249—250° (corr.). The three aminoflavones have been diazotised and coupled with β-naphthol to form *flavoneazo-β-naphthols*, m. p. 265—266·5°, 257°, and 274—275° (corr.) respectively, giving

orange to red shades on silk and wool, extremely fast to light and alkalis. Other compounds obtained are *2′-acetoxyflavone*, m. p. 88·5—89° (corr.), *2′-diacetylaminoflavone*, m. p. 186·5—187·5° (corr.), *3′-diacetylaminoflavone*, m. p. 231—232° (corr.), *4′-diacetylaminoflavone*, m. p. 246—248° (corr.), *β-phenoxy-β-phenylpropionic acid*, m. p. 150—151° (corr.), the *barium* salt of a disulphonic derivative of the latter acid, and *methyl β-bromo-β-phenylpropionate*, m. p. 37·5—38·5° (corr.). It is noted that whereas all the hydroxyflavones are colourless, all the aminoflavones are yellow, thus indicating the more powerful auxochromic effect of the amino-group in this series; also 4′-aminoflavone possesses the remarkable property of fluorescence only in neutral solvents which contain the hydroxyl group. J. F. B.

Carnosine, Constitution and Synthesis. GEORGE BARGER and FRANK TUTIN (*Biochem. J.*, 1918, **12**, 402—407).—2:4:5-Trinitrotoluene condenses with amino-acids when boiled in dilute alcoholic solution, the amino-acid becoming attached to the benzene ring by its amino-group, which replaces the reactive nitro-group in position 5. This reaction does not occur with imino-groups, but does take place with the free amino-groups of peptides. The condensation product of 2:4:5-trinitrotoluene with carnosine on hydrolysis yields dinitrotolyl-β-alanine, thus proving carnosine to be β-alanylhistidine,

$$\begin{matrix} NH\cdot CH \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot NH_2.$$

For the synthesis of carnosine, *β-nitropropionyl chloride*, b. p. 123°/10 mm., was condensed with histidine methyl ester, and the resulting very unstable product was at once reduced by stannous chloride and dilute hydrochloric acid, and the carnosine isolated as its copper salt. W. G.

The α- and β-Hydroxydihydrocinchonines and their Rôle in the Production of certain Isomerides of Cinchonine. E. LÉGER (*Compt. rend.*, 1919, **168**, 404—407).—The so-called β-hydroxycinchonine, like its α-isomeride (compare A., 1918, i, 304), when acted on by 50% sulphuric acid gives a mixture of cinchonigine, cinchoniline, and *apo*cinchonine. The ratio of cinchonigine to cinchoniline obtained from the β-isomeride is practically the inverse of that obtained from the α-isomeride, but if the strength of the acid is increased to 70% and the heating prolonged to twenty-four hours, the proportions of these two bases are almost the same from each isomeride. From this, the author concludes that β-hydroxycinchonine, like the α-isomeride (*loc. cit.*), is a product of the addition of the elements of water to cinchonine, the two isomerides containing, respectively, the groupings

$$\underset{\alpha.}{\begin{matrix} \;\;\;H \;\;\; / \\ CH_3\cdot\dot{C}{-}CH \\ \;\;\dot{O}H \;\; | \end{matrix}} \qquad \text{and} \qquad \underset{\beta.}{\begin{matrix} \;\;\;OH \;\; / \\ CH_3\cdot\dot{C}{-}\dot{C}H \\ \;\;\dot{H} \;\;\; | \end{matrix}}$$

W. G.

Nicotinic Acid Derivatives. II. Guvacine and *iso*Guvacine. E. WINTERSTEIN and A. B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1918, **104**, 48—53. Compare A., 1918, i, 35).—In view of recent publications on the same subject (Hess and Liebbrandt, A., 1918, i, 401; Hess, *ibid.*, 403; Freudenberg, *ibid.*, 403), the authors submit a short account of their experiments, fuller details being promised in a later paper. They are led to the conclusion that guvacine is in all probability Δ^3-tetrahydronicotinic acid (contrast Trier, A., 1913, i, 803), whereas *iso*guvacine is a simple derivative of pyrrole.

The following details are given. Guvacine crystallises in prisms, m. p. 293—295°, is neutral to litmus, and optically inactive. The hydrochloride, platinichloride, and aurichloride have m. p.'s 312°, 233°, and 195—197° respectively; nitrosoguvacine forms needles, m. p. 167°. Reduction of guvacine with hydrogen in the presence of platinum leads to the formation of dihydroguvacine, m. p. 252° (hydrochloride, m. p. 237°; platinichloride, m. p. 233—235°; aurichloride, prismatic needles, m. p. 193—195°; mercurichloride, m. p. 230—231°), which is shown to be identical with hexahydronicotinic acid. Methylation of guvacine leads to the formation of *N*-dimethylguvacine, m. p. 225° (?) [hydrochloride, m. p. 256—258°; platinichloride, m. p. 253°; aurichloride, m. p. 224—226°; picrate, m. p. 224—225°; mercurichloride, m. p. 174—176°], which is found to be identical in all respects with the arecaidinemethylbetaine described by Willstätter (A., 1897, i, 385).

*iso*Guvacine has m. p. 220°, is faintly acid to litmus, and is optically inactive. The hydrochloride, m. p. 231° (decomp.), platinichloride, m. p. 235° (decomp.), and aurichloride, m. p. 198—200°, are described. When the base is heated with zinc dust, an intense odour of pyrrole is observed, and a pine shaving dipped in concentrated hydrochloric acid is coloured intensely red. *iso*Guvacine is slowly reduced by hydrogen in the presence of platinum, but the hydrochloride of the new base is not uniform; the platinichloride has m. p. 225°. *iso*Guvacine forms a dimethyl derivative, the platinichloride of which has m. p. 252°. H. W.

Ring Formation with Elimination of a Nitro-group. S. REICH and (MLLE.) V. NICOLAEVA (*Helv. Chim. Acta*, 1919, **2**, 84—88).—The reaction examined by Reich with Gaigailian (A., 1917, i, 595) and with Turkus (*ibid.*, i, 585) has been further studied. Whilst the phenylhydrazones of ethyl 2:4-dinitrophenylglyoxylate, of 2:6-dinitrobenzaldehyde, and of 2-chloro- or 2-bromo-6-nitrobenzaldehyde yield *iso*indazole derivatives with the loss of a nitro-group under the influence of alkali, 2:4-dinitrobenzaldehydephenylhydrazone remains unchanged by similar treatment. To test the theory that this difference in behaviour is sterically due to the accumulation of atoms and atomic groups round the aldehydic carbon atom, 2:4-*dinitroacetophenonephenylhydrazone*, reddish-brown needles, m. p. 165—166°, has been pre-

pared from 2:4-*dinitroacetophenone*, an oil which is obtained by hydrolysing its *oxime*, yellow prisms, m. p. 124°, with warm 15% hydrochloric acid. The oxime is obtained in 20—30% yield by the action of amyl nitrite and sodium ethoxide on 2:4-dinitroethylbenzene, the main product of this reaction, however, being 5-*nitro-2-methylindoxazen*, $NO_2{\cdot}C_6H_3{<}{}^{CMe}_{O}{>}N$, yellow crystals, m. p. 114°.

In accordance with the theory above, 2:4-dinitroacetophenonephenylhydrazone is converted by treatment with cold aqueous-alcoholic sodium hydroxide into 6-*nitro*-1-*phenyl*-3-*methyliso-indazole*, $NO_2{\cdot}C_6H_3{<}{}^{NPh}_{CMe}{>}N$, yellow spangles, m. p. 139—140°.

C. S.

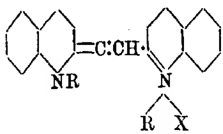
Thienylquinolinecarboxylic Acid. MAX HARTMANN and ERNST WYBERT (*Helv. Chim. Acta*, 1919, **2**, 60—63).—2-2′-*Thienylquinoline-4-carboxylic acid*, $C_4H_3S{\cdot}C_9H_5N{\cdot}CO_2H$, yellow leaflets, m. p. 211°, is obtained by heating 2-thienyl methyl ketone, isatin, 28% potassium hydroxide solution and alcohol on the water-bath for three hours and acidifying the cooled solution with acetic acid. By repeated recrystallisation the acid is obtained in colourless crystals having the same m. p., but by solution in alkali and reprecipitation by acid the yellow modification is regenerated. The *ethyl* ester, colourless needles, has m. p. 83°. The salts of the acid are extremely soluble in water, forming solutions having a neutral reaction.

The acid resembles, but exceeds, 2-phenylquinoline-4-carboxylic acid in its antiphlogistic and analgesic action. When fed to an animal or when injected in the form of a soluble salt into the blood system it produces in the animal a violet-red colour and the urine acquires the colour of concentrated potassium permanganate solution. The colouring matter, which is very persistent and appears in almost all the internal organs, can be isolated from the urine and is obtained in small crystals (C=56·51; H=4·57; N=5·41; S=7·31%. Mol. wt. in freezing naphthalene=2207). The substance has pronounced acid properties, exhibits none of the colour reactions typical of thiophen, and cannot be produced from the thienylquinolinecarboxylic acid in the laboratory. C. S.

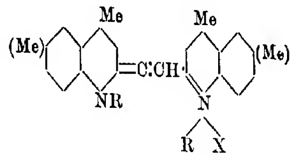
Nitro-, Arylazo-, and Amino-glyoxalines. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1919, **115**, 217—260).

Quinocyanines (Pinacyanoles, Dicyanines). OTTO FISCHER (*J. pr. Chem.*, 1918, [ii], **98**, 204—232).—Little has hitherto been known of the blue cyanines which have been put on the market under the names pinacyanole chloride, dicyanine bromide, and ψ-dicyanine iodide, and are stated to be the best sensitisers in photography. Considerable light is now thrown on the conditions of their formation. For the production of pinacyanoles and of their homologues, the ψ-dicyanines obtained from 2:4-di- and 2:4:6-trimethylquinoline alkyliodides, two quinoline molecules are necessary,

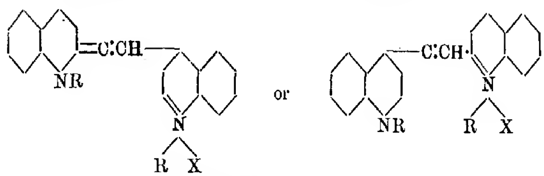
each containing a methyl group in position 2, by means of which the two molecules are united together. For the production of dicyanines are necessary two quinoline molecules, one containing a methyl group in position 2 and the other a methyl group in position 4:



(Pinacyanole.)



(ψ-Dicyanines.)



(Parent substance of dicyanine.)

In the formulæ R=Me or Et and X=halogen.

The chromophore of the *iso*cyanines (for example, ethyl-red) contains two, that of the pinacyanoles three, and that of the dicyanines four double linkings, which accounts for the deepening of the colours from violet-blue through blue to greenish-blue.

[With (Frl.) C. Bauer, (Frl.) P. Merkel, and G. Scheibe].—The simplest pinacyanole, quinaldine-blue (formula given above), was prepared (Farbwerke vorm. Meister, Lucius & Brüning, D.R.-P. 172118) by boiling an alcoholic solution of quinaldine ethiodide, with or without quinoline ethiodide, with aqueous sodium hydroxide in the presence of formaldehyde. At first it was believed that two different blue pinacyanoles were formed, but it is now shown that only one is obtained, the quinoline ethiodide taking no part in the reaction. It is also shown that the presence of formaldehyde (or, as stated in the patent claim, of glyoxylic acid, iodoform or chloroform), although advantageous, is not essential, provided air or other oxidising agent, such as potassium ferricyanide or ammonium persulphate, is present. It is true that in the case of quinoline derivatives unsubstituted in position 4 the latter methods result chiefly in the production of *iso*cyanines, but when position 4 is occupied by a methyl or phenyl group the product is chiefly the pinacyanole.

In addition to the iodide (quinaldine-blue), m. p. about 276—278° (decomp.), the bromide, m. p. about 274—275° (decomp.), chloride, m. p. about 263° (decomp.), picrate, decomp. about 250—260°, *platinichloride*, *aurichloride*, and *mercurichloride* are described, and also the additive compounds of the iodide and bromide respec-

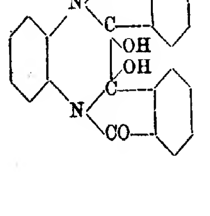
tively with bromine. Attempts to find evidence of the presence of a ruptured ring by testing for the presence of a secondary amine gave negative results. By oxidation with an excess of alkaline potassium ferricyanide solution, pinacyanole chloride yields 1-ethyl-quinolone.

Many attempts were made to convert ethyl-red and its homologues into pinacyanoles by means of formaldehyde, but the violet-blue substances obtained showed no similarity at all to the pinacyanoles.

By boiling an alcoholic solution of 2:4-dimethylquinoline ethiodide and potassium hydroxide ($\frac{1}{2}$ mol.) in a current of air a mixture of several colouring matters is produced, from which the ψ-dicyanine iodide, $C_{26}H_{27}N_2I$ (formula above), and the dicyanine iodide (formula above) have been isolated in the form of the corresponding bromides. When 4-phenyl-2-methylquinoline methiodide is similarly treated in methyl-alcoholic solution, no dicyanine is formed, but the ψ-dicyanine, 4:4′-*diphenylpinacyanole iodide*, $C_{34}H_{27}N_2I$, crystals containing CH_4O (*picrate*, almost black, crystalline powder), is obtained. A similar result is obtained in the case of 4-phenyl-2:6-dimethylquinoline methiodide, but 2:4:6-trimethylquinoline ethiodide, which again contains a methyl group in position 4, yields both the *ψ-dicyanine iodide* (chief product) and the *dicyanine iodide*. The former, $C_{28}H_{31}N_2I$, green prisms containing C_2H_6O, forms blue solutions which appear reddish-violet in thin layers (*picrate*, dark green leaflets), whilst the latter, $C_{28}H_{31}N_2I$, forms green needles (*picrate*, greenish-black needles; *bromide*, green needles).

The various classes of cyanines are differentiated by their absorption spectra. C. S.

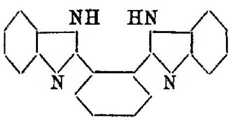
Condensation of Aromatic *ortho*Diamines with Phthalic Anhydride. HANS LIEB (*Monatsh.*, 1918, **39**, 873—895).—It has been shown by Edlbacher that diphthalyl-*o*-phenylenediamine, $C_6H_4N_2[(CO)_2C_6H_4]_2$, can be reduced by zinc dust and acetic acid to a substance, m. p. 275—277° (decomp.), which, at its melting point, passes into a red, crystalline product, $C_{22}H_{12}O_2N_2$, m. p. 278°. The present communication deals with the constitution of these substances, the elucidation of which in the first case is greatly hampered by the difficulty of eliminating solvent of crystallisation. The author, however, considers the material to be 1:2:3:4-dibenzoylene-1:2:3:4-tetrahydro-2:3-dihydroxyquinoxaline (annexed formula), whilst the substance, $C_{22}H_{12}O_2N_2$, is 1:2:3:4-dibenzoylene-1:4-dihydroquinoxaline. Similar substances may be obtained from phthalic anhydride and 1:2-naphthalenediamine.



Diphthalyl-o-phenylenediamine, m. p. 297°, is obtained in 45% yield by heating a mixture of phthalic anhydride and

o-phenylenediamine, and is reduced to 1:2:3:4-*dibenzoylene-2:3-dihydroxy*-1:2:3:4-*tetrahydroquinoxaline*, which separates from glacial acetic acid ($+1C_2H_4O_2$) in yellow prisms, and from aqueous alcohol ($+H_2O$) in indefinite, crystalline aggregates. The m. p. is not sharp, the substance becoming red at above 260° and yielding an intensely red, molten mass at 274—278° with brisk evolution of gas. Attempts to prepare an acetyl or benzoyl derivative, an oxime or a hydrazone were unsuccessful, but the action of methyl sulphate yielded a *monomethyl* ether, $C_{23}H_{16}O_4N_2,H_2O$, m. p. 190°, after softening and evolving gas from 170°. 1:2:3:4-*Dibenzoylene*-1:4-*dihydroquinoxaline* crystallises in intensely red needles, m. p. 278°; it slowly dissolves in concentrated alcoholic potassium hydroxide, and the solution, on acidification, yields a substance which at 270—273° is reconverted into the red product, but which, in spite of its close similarity, is not identical with the original material.

Attempts to prepare the red substance from biphthalyl and o-phenylenediamine were not successful, the product obtained being *o-phenylenedibenziminazole* (annexed formula), colourless needles, m. p. 425° (decomp.), which was also prepared by condensing dihydrodiphthalyl with o-phenylenediamine or from the amine and phthalic anhydride at 290° in a sealed tube. The corresponding *acetyl* and *benzoyl* derivatives have m. p.'s 198—199° after softening at 195° and 229—230° after softening at 225° respectively.



The following derivatives have been obtained from 1:2-naphthylenediamine: *diphthalyl*-1:2-*naphthylenediamine*, rhombohedra or hexagonal prisms, m. p. 282°, which on reduction gives the *product*, $C_{26}H_{16}O_4N_2$, m. p. 280—284°, with evolution of gas and formation of a red mass, and 1:2:3:4-*dibenzoylene*-1:4-*dihydro*-5:6-(7:8)-*benzquinoxaline*, red needles, m. p. 323—324°, after sintering at 321°. During the preparation of the first-named substance, 1:2-*naphthylenebenziminazole-o-carboxylic acid*, leaflets, m. p. 304—305°, is obtained as by-product; this is converted by acetic anhydride into *benzoylenenaphthiminazole*, $C_{18}H_{10}ON_2$, orange-yellow needles, m. p. 213°. H. W.

Proteins. I. Preparation of Ovalbumin Solutions of well-defined Composition, and the Analytical Methods used. S. P. L. Sörensen [with Margrethe Höyrup] (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 1—11, 12—67; *Zeitsch. physiol. Chem.*, 1918, **103**, 1—14, 15—79).—The crystals of ovalbumin are prepared by the Hopkins and Pinkus' method, and after being recrystallised six times are free from ash, conalbumin, and mucoid. By means of a dialysing apparatus described in detail, solutions of ovalbumin may be completely freed from sulphate and almost entirely freed from ammonia. The content of water, ammonia,

and sulphuric acid in the crystals of ovalbumin is derived by the application of the "principle of proportionality," according to which, if an ovalbumin solution is precipitated by ammonium sulphate and the crystalline precipitate subsequently filtered off, and if weighed parts of the filtrate as well as of the precipitate with the adherent mother liquor are analysed, it is possible from the results of the analyses to draw certain conclusions regarding the composition of the precipitate on the presumption that the mother liquor surrounding the precipitate has the same composition as the filtrate.

H. W. B.

Proteins. II. Capacity of Ovalbumin to Combine with Acids or Bases. S. P. L. SÖRENSEN [with MARGRETHE HÖYRUP, JENNY HEMPEL, and S. PALITZSCH] (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 68—163; *Zeitsch. physiol. Chem.*, 1918, **103**, 104—210).—From theoretical considerations it is possible to calculate the hydrogen-ion concentration in an aqueous salt solution containing an excess of an acid or base corresponding with the salt. By an extension of the method, formulæ are deduced which permit of the calculation of the hydrogen-ion concentration of solutions of ampholytes containing small amounts of free acid, account being taken of the dissociation of the ampholyte into hydrogen- and ampholyte-anions and into hydroxyl and ampholyte cations respectively. The effect of the addition of salts is then considered, and it is found that at hydrogen-ion concentrations which are not in the neighbourhood of the isoelectric point of the ampholyte the capacity to combine with acids is (*a*) independent of the concentration of the ampholyte, (*b*) increased by increasing the concentration of the salt, (*c*) positive at hydrogen-ion concentrations superior to that corresponding with the isoelectric point of the ampholyte, and negative (that is, the ampholyte is combined with surplus base) at hydrogen-ion concentrations inferior to it. After testing the accuracy of these formulæ by application to solutions of amino-acids and salts, they are applied to solutions of ovalbumin, and it is found that the capacity of the ovalbumin to combine with acids is independent of the concentration of the ovalbumin at hydrogen-ion concentrations which are greater or smaller than that corresponding with the isoelectric point of the ovalbumin provided the concentration of ammonium sulphate is constant. It is further increased by increasing the concentration of the ammonium sulphate. At the isoelectric point the capacity of the ovalbumin to combine with acids is to some extent dependent on its concentration. By reference to a curve, the slight excess of sulphuric acid present in a solution of ovalbumin containing ammonium sulphate may be calculated, and also the method of its distribution between the two phases of the ovalbumin solution, namely, the dispersed phase consisting of hydrated ovalbumin and the external phase of ammonium sulphate and water. From these considerations the isoelectric point of ovalbumin is found to be at about $15{\cdot}74 \times 10^{-6}$ H. W. B.

Proteins. III. Composition and Properties of Ovalbumin Separated in Crystalline Form by means of Ammonium Sulphate. S. P. L. SÖRENSEN and MARGRETHE HÖYRUP (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 164—212; *Zeitsch. physiol. Chem.*, 1918, **103**, 211—266. Compare preceding abstracts).—By the application of the principle of proportionality, it is found that the crystals of ovalbumin contain water to the extent of about 0·22 gram of water per 1 gram of ovalbumin. The amount of water present is independent of the conditions of crystallisation (time and temperature of crystallisation, concentrations of ammonium sulphate, protein, and hydrogen ions). It is similarly found that if the crystallisation takes place at a hydrogen-ion concentration of about 13×10^{-6}, the crystals contain neither surplus sulphuric acid nor ammonia; at higher hydrogen-ion concentrations, the crystals contain surplus sulphuric acid, at lower concentrations they contain surplus ammonia. A consideration of the character of the crystallisation process leads the authors to the conclusion that the crystallisation of ovalbumin is simply the crystallisation of a supersaturated solution of a substance crystallising slowly and with difficulty.

In a postscript, it is announced that successful crystallisations of ovalbumin have been obtained by means of a mixture of ammonium and diammonium phosphates instead of ammonium sulphate. The crystals so obtained closely resemble those prepared in the usual manner. H. W. B.

Proteins. IV. State of Equilibrium between Crystallised Ovalbumin and Surrounding Mother Liquor, and the Applicability of Gibbs's Phase Rule to such Systems. S. P. L. SÖRENSEN and MARGRETHE HÖYRUP (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 213—261; *Zeitsch. physiol. Chem.*, 1918, **103**, 267—323. Compare preceding abstracts).—The relations existing between crystallised ovalbumin and the surrounding mother liquor are in conformity with those associated with a heterogeneous system containing one solid phase, hydrated ovalbumin, and three other components, water, ammonia, and sulphuric acid. The system in all essential features is conformable to Gibbs' phase rule. At the equilibrium point, the content of ovalbumin in the mother liquor is smaller as the concentration of ammonium sulphate increases. The hydrogen-ion concentration at which the concentration of ovalbumin in the mother liquor is at a minimum corresponds with $p_H = 4·58$, and seems to be independent of the concentration of ammonium sulphate and the temperature of crystallisation. Similarly, the optimum temperature is at about 20°; but little variation is observed between the limits of 12° and 29°.

The velocity of crystallisation increases with the concentration of ammonium sulphate, with the initial concentration of protein, and with the temperature of crystallisation. H. W. B.

Proteins. V. Osmotic Pressure of Ovalbumin Solutions. S. P. L. SÖRENSEN [with J. A. CHRISTIANSEN, MARGRETHE HÖYRUP, S. GOLDSCHMIDT, and S. PALITZSCH] (*Compt. rend. trav. Lab. Carlsberg*, 1918, **12**, 262—372. Compare preceding abstracts).—The osmometer used consists essentially of a collodion cap serving the purpose of a semi-permeable membrane and containing the ovalbumin solution employed as inner liquid, the outer liquid being an ammonium sulphate solution in diffusion equilibrium with the dispersion medium of the inner liquid. The osmotic pressure is measured by determination of the counter-pressure required to be exerted on the surface of the inner liquid to prevent a migration of the liquids through the membrane. On increasing the concentration of ammonium sulphate, the osmotic pressure of the ovalbumin is depressed. This result is explained by assuming that the increased amount of ammonium sulphate favours the condensation of two or more hydrated ovalbumin particles into a single particle by means of the bivalent sulphate group.

The osmotic pressure does not undergo any material alteration when the hydrogen-ion concentration is varied between 40×10^{-6} and 100×10^{-6}; at higher concentrations, the pressure increases very slowly with the hydrogen-ion concentration, whilst at concentrations inferior to 40×10^{-6}, it increases rapidly as the concentration decreases. These results are also accounted for by the assumption of a condensation process promoted by the sulphate group.

From the various results which have been so far obtained, the number of nitrogen atoms contained in a single non-condensed ovalbumin particle is estimated at approximately 380; hence the molecular weight of anhydrous ovalbumin appears to be about 34,000. Taking into account the results obtained indicating the amount of sulphuric acid contained in the crystallised ovalbumin, the albumin crystals seem to consist normally of two albumin particles bound together by three molecules of sulphuric acid.

H. W. B.

Proteins of Cow's Colostrum. I. The Relation between the Euglobulin and ψ-Globulin of Cow's Colostrum. HAROLD WARD DUDLEY and HERBERT ERNEST WOODMAN (*Biochem. J.*, 1918, **12**, 339—351).—The authors have studied the optical properties of euglobulin and ψ-globulin of cow's colostrum when dissolved in $N/2$- and $N/4$-sodium hydroxide, and also the optical properties of the amino-acids derived from the hydrolysis of "racemised" colostrum euglobulin and ψ-globulin. The results obtained support the view that these two substances are structurally identical in so far as the protein portion of the molecule is concerned.

W. G.

Some Metallic Compounds of Hæmatoporphyrin. JOHN ALEXANDER MILROY (*Biochem. J.*, 1918, **12**, 318—338).—The author has prepared the compounds of hæmatoporphyrin with zinc, cadmium, nickel, cobalt, iron, copper, tin, and lead, has described their absorption spectra, and determined their resistance to the

action of mineral acids and the resistance of the absorption bands of the pigments to dilution.

The stannous compound may be prepared directly from blood or hæmatin, and on this is based a delicate test for the detection of traces of blood pigment. The stained tissue, where blood is suspected, is boiled with a little glacial acetic acid in a small test-tube. To the boiling solution, three drops of $2M$-stannous chloride solution are added, and the solution is boiled for one minute. After filtering off the precipitate formed, the absorption bands of acid hæmatoporphyrin can easily be seen. A small quantity of solid sodium acetate is then added, and the solution is again boiled. The fluid, which is now bright red, is cooled and filtered, and the filtrate shows the two characteristic absorption bands of the stannous derivative. A method is given for extracting the blood pigment with phenol prior to this examination, and it is claimed that, by this means, it is possible to detect blood pigment at a dilution of $10^{-6} \times M/5$. W. G.

Pyrrole Reaction of the true Nucleic Acids. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1918, **104**, 1).—A pine shaving moistened with concentrated hydrochloric acid is coloured carmine-red by the vapours obtained by heating a dry mixture of sodium nucleate and ammonium chloride; the reaction is not shown by sodium nucleate alone. Since furan derivatives are readily converted into derivatives of pyrrole by dry distillation with ammonium salts, the author regards the reaction as a confirmation of his theory (A., 1914, i, 1098; 1918, i, 85) that the carbohydrate group of the true nucleic acids belongs to the furan type. H. W.

Mutarotation of Gelatin and its Significance in Gelatinisation. C. R. SMITH (*J. Amer. Chem. Soc.*, 1919, **41**, 135—150).—In solution, gelatin exhibits mutarotation, and a study of the influence of changes of temperature on this mutarotation shows that in aqueous solution two forms of gelatin probably exist, one, termed the sol form A, stable above 33—35°, and the other, called the gel form B, stable below 15°. Between these temperatures, the two forms exist in equilibrium, and the mutarotation appears to be due to the transformation of the one form into the other by a reaction reversible with the temperature. This reaction is apparently bimolecular, that is, of the type to be expected if two molecular or equivalent weights of form A combine to form one molecular weight of form B. The relationship between the percentage quantities of the two forms when equilibrium is established at any given temperature between 17° and 33° seems to be represented by the equation $(a-x)^2/x=K$, in which a is the difference (about 1·2) between the rotations produced by 1 gram of gelatin per 100 c.c. in a tube 100 mm. long at 33—35° and at 17°, x is the difference between the rotations at 33—35° and at the given temperature, and K is a constant. Increase in lævorotation, indicating increasing formation of the gel form B, follows closely increase in viscosity.

A definite proportion of form *B* is necessary to form a jelly of standard viscosity, and this proportion, slightly increased as concentration increases, produces the standard viscosity in gelatin solutions of much higher concentrations. Maximum gelatinisation temperatures or melting points approach the limiting value, 33—35°, as the concentration of gelatin increases. At these maximum temperatures, gelatinisation is produced by the presence of a certain definite minimum proportion of form *B* required for the formation of a jelly; above 35°, gelatinisation does not take place at any concentration.

The existence of two forms of gelatin, on which gelatinisation of the solutions is dependent, is confirmed by the behaviour of such solutions with alcohol, which at temperatures below 30° either precipitates the gelatin or renders the solutions opalescent if present to the extent of 15%; if the concentration of the gelatin is high, alcohol precipitates an opalescent jelly. Above 35°, the precipitation requires far larger proportions of alcohol (45—50%), unless a comparatively large amount of an electrolyte is also added. Further confirmation is afforded by the results of measurements of osmotic pressure (compare Moore and Roaf, A., 1907, ii, 73), viscosity (von Schroeder, A., 1903, ii, 721), and "gold numbers" (Menz, A., 1909, i, 343).

Gelatin sols dried at above 35° and gels dried at below 15° give different solid forms, and whilst the solid gelatin thus obtained may or may not be in the form in which it exists in the material from which it is prepared, there is some indication that the solid gelatin prepared by drying sols above 35° is the form existing in the sols. T. H. P.

Pepsin. I. Chemical Changes in the Purification of Pepsin. LEWIS DAVIS and HARVEY M. MERKER (*J. Amer. Chem. Soc.*, 1919, **41**, 221—228).—The purification of commercial pepsin by fractional precipitation, salting-out, filtration, and dialysis is accompanied by gradual elimination of the secondary protein derivatives, including amino-acids, the purified samples tending more and more to approach the proteins in character as the proteolytic activity increases; the proportion of material coagulable by heat also increases. The fact that the most active samples respond strongly to Molisch's test indicates the possibility that the pure enzyme may be a conjugated protein, probably a gluco-protein. The proportion of mineral matter present also diminishes continuously as purification proceeds; the sulphur and calcium appear, however, to be unaffected, although the phosphorus content shows a marked decrease and chlorides are apparently eliminated entirely. Other than the increase resulting from removal of non-nitrogenous impurities, there is little apparent change in the proportion of total nitrogen.

The diminution in the α-amino-acid content is almost proportional to the increase in proteolytic activity, and the small amount of α-amino-acid in the most active sample, which exhibits an almost neutral reaction, appears to correspond with lysine. It seems probable that the concentration of hydrogen ions in solutions of the

pure enzyme, could this be obtained, would be comparable with the low values given by other proteins.

The optical activities of the enzymes of different degrees of purity were measured, but the same values were obtained with pepsins showing different proteolytic activities. The rennetic activities correspond closely with the proteolytic activities.

T. H. P.

A Delicate Method of Determining Invert Activity. C. K. WATANABE and V. C. MYERS (*Proc. Soc. Exp. Biol. Med.*, 1918, 15, 142—143; from *Physiol. Abstr.*, 1919, **3**, 502).—The method is similar to that advocated by Myers and Killian (compare A., 1917, i, 369) for measuring diastatic activity, but in this case sucrose solution is substituted for the solution of soluble starch or glycogen.

W. G.

Influence of Hydrogen-ion Concentration on the Enzymic Activity of Three Typical Amylases. H. C. SHERMAN, A. W. THOMAS, and M. E. BALDWIN (*J. Amer. Chem. Soc.*, 1919, **41**, 231—235).—The enzymes examined were the amylases of pancreas, malt, and *Aspergillus oryzae*, representing the starch-splitting enzymes of the higher animals, higher plants, and fungi respectively. Experiments were made to determine as definitely as possible the hydrogen-ion concentrations which induce optimal activity of the pancreatic and fungus amylases, and to establish for each of the three amylases the limits of hydrogen-ion concentration within which any enzymic activity is shown and the form of the curve representing the activities at all concentrations of the hydrogen ion between these limits. The experimental methods used were those previously described (A., 1915, i, 183), except that greater precautions were taken to prevent any action of light during the enzymic actions, and that, in measuring the hydrogen-ion concentration by the electrometric method, the current of hydrogen was replaced by a Clark cell and a rocking electrode.

The results of Sherman and Thomas (*loc. cit.*) on the optimum hydrogen-ion concentration for malt amylase were confirmed and that for pancreatic amylase more sharply defined; that for the maltase of *Aspergillus oryzae* is closer to the value for malt amylase than to that for the pancreatic enzyme. The latter is active for values of P_H 4—10, the optimal activity being at about 7; the solutions commonly considered neutral show under similar conditions the value 5·8 for P_H. Malt amylase is active for P_H=2·5—9, the optimal activity being at 4·4—4·5, whilst with the *Aspergillus* enzyme the limits of P_H are 2·6 and 8 and the optimum 4·8. The influence of the concentration of the electrolyte, as distinguished from the concentration of the hydrogen ion alone, appears to be greatest with pancreatic amylase and least with the amylase of *Aspergillus oryzae*.

T. H. P.

Effect of Neutral Salts on the Activity of Ptyalin. ELBERT W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1919, **41**, 228—230).—The

methods used in this investigation were essentially those previously described (A., 1917, i, 358; 1918, i, 274). Ammonium chloride and nitrate, and, to a less extent, the sulphate and thiocyanate, enhance the hydrolytic action of ptyalin on starch. The effects of the ammonium salts of organic acids are much smaller; the acetate, but not the oxalate, shows some power as an auxo-amylase, whilst the tartrate exerts a slight stimulating action. Ammonium chloride and bromide produce marked increase in the amount of starch hydrolysed, the quantity of reducing products being the same in each case; the fluoride inhibits the action. Similar results are obtained with the sodium haloids. The effect of sodium chloride is not altered by changing the cation to potassium or calcium, so that the action of a salt is a function, not of the cation, but of the anion. The tervalent cations were not tested, owing to the coagulating effect of their soluble salts on colloids.

Tests made by means of Nessler solution at intervals during the action of ptyalin on starch in presence of an ammonium salt show that the ammonium ion is not destroyed during the digestion.

T. H. P.

Photochemical Effect of certain Fluorescent Substances on Rennin. Janet H. Clark (*Amer. J. Physiol.*, 1918, **47**, 251—264; from *Physiol. Abstr.*, 1919, **3**, 502).—The inhibition of rennin by light is attributed to the formation of toxic substances as a result of photochemical action. This may be accompanied by fluorescence, and fluorescence may or may not be accompanied by the formation of toxic substances. Free halogens are the toxic substances in the experiments described with eosin and erythrosin.

W. G.

Simple Method of Making *p*-Arsanilic Acid. Philip Adolph Kober and Walter S. Davis (*Proc. Soc. exp. Biol. Med., New York*, 1918, **16**, 13—15).—1000 C.c. of crude 75% arsenic acid are concentrated to about 100 c.c. by heating for twelve to fifteen hours in an open beaker in an oil-bath at 120—140°. After cooling, the acid is slowly added, with vigorous stirring, to 1400 c.c. of dry aniline, at or below 0°. The mixture becomes viscous, then granular, and is finely ground. 200 Grams of it are heated in a flask and stirred until the powder melts; it is then heated for one and a-half hours at 160—170° and one hour at 180—183°, under a reflux condenser. After cooling, 450 c.c. of 3*N*-hydrochloric acid are added, the aniline is separated off, the solution is shaken with 15—20 grams of kaolin or infusorial earth, and filtered with aid of suction. To the clear filtrate, 100 c.c. of 6*N*-hydrochloric acid are added, and then, on an aliquot portion, the further amount of hydrochloric acid is determined by trial, which will give the maximum crystallisation on keeping. This, added to the main bulk, yields 30% of crystalline primary arsanilic acid, without any secondary acid. The usual mistake in the laboratory is to employ too much aniline and too high a temperature.

G. B.

Method of Preparing Pure Dihydrochloride of Diaminodihydroxyarsenobenzene [Salvarsan]. PHILIP ADOLPH KOBER (*Proc. Soc. exp. Biol. Med., New York*, 1918, **16**, 23—24).—The author dislikes the precipitation of the dihydrochloride from methyl alcohol by ether, and prefers the mass action of strong hydrochloric acid in aqueous solution. The alkaline solution of the base is slightly acidified with hydrochloric acid, and the solution is poured slowly, with vigorous stirring, at a low temperature into hydrochloric acid (1 in 1, or more dilute). This obviates coagulation of the flocculated particles.

G. B.

Halogenation. XVII. Action of Halogens on the Grignard Reagent and Replacement of Halogen Atoms by one another. RASIK LAL DATTA and HARAPARBUTTY KUMAR MITTER (*J. Amer. Chem. Soc.*, 1919, **41**, 287—292).—Few investigations have been made on the action of halogens on the Grignard reagent. The authors find that one halogen is, in general, able to displace other halogens from the Grignard reagent with the production of the corresponding haloid derivatives, the yield of the latter being greatly influenced by the nature of the halogen and by the experimental conditions; the reaction is sometimes accompanied by secondary reactions due to the union of the Grignard residues.

When iodine is added to magnesium phenyl bromide, the resultant products are iodobenzene in 25—30% yield, benzene in 30—40% yield, and a small proportion of diphenyl, but addition of magnesium phenyl bromide to ethereal iodine solution gives phenyl iodide in 90% yield. By the action of iodine on magnesium phenyl iodide, iodobenzene, benzene, and diphenyl are formed, the last constituting the main product. The action of iodine on magnesium *o*-tolyl bromide gives *o*-iodotoluene in 80% yield. From *m*-bromotoluene, *m*-iodotoluene is similarly obtained in 76% yield, as well as a little unchanged *m*-bromotoluene; from *p*-bromotoluene, in addition to a little unchanged substance, *p*-iodotoluene is formed in 74% yield. By the action of iodine on magnesium ethyl iodide, ethyl iodide in low yield is obtained.

Similarly, in the action of bromine on magnesium phenyl iodide, benzene and bromobenzene are the principal products, the yield of the latter being 30—40%; a small proportion of diphenyl is also obtained. From magnesium phenyl bromide, bromobenzene is obtained in 30—40% yield. By the action of bromine on magnesium ethyl iodide, ethyl bromide is formed, and from magnesium *n*-propyl iodide, propyl bromide is formed in 30—40% yield.

The action of chlorine on magnesium phenyl bromide gives a product which explodes with great violence when shaken. From *p*-bromotoluene, *p*-chlorotoluene is obtained in 20% yield.

T. H. P.

Physiological Chemistry.

The Coagulation of Blood. MARIO CHIÒ (*Arch. Farm. sperim.*, 1918, **25**, 175—192, 193—212; from *Chem. Zentr.*, 1918, ii, 1048).—The behaviour towards hydrochloric acid and carbon dioxide (A., 1917, i, 672) varies with the season of the year in such a manner that, during the warmer months, smaller concentrations of hydrochloric acid are sufficient to prevent the coagulation of the salt plasma, whilst, on the other hand, higher tensions of carbon dioxide are necessary. It is advisable, although not absolutely necessary, to perform the experiments at constant temperature. New experiments have shown that a displacement of the chemical equilibrium in dilute salt plasma occurs, which is shown by an increase in alkalinity. Hydrolysis of fatty matter must, among other influences, be a cause and consequence. Hydrolytic fission of alkali soaps liberates fatty acids, which yield calcium soaps in the presence of soluble and dissociable calcium salts. Changes therefore occur in the condition of certain colloids, which result first in the formation of gels and subsequently in contraction, owing to diminution in the irrigation of the lipoid–albumin complexes. Increase in the tension of carbon dioxide diminishes the rate of this phenomenon. The coagulation of blood may be explained by the formation of calcium soaps by a process which can be limited or prevented by suitable adjustment of the carbon dioxide tension both outside and within the organism. H. W.

Proteolytic Relationships in the Serum of the Horse and Ox. S. G. HEDIN (*Zeitsch. physiol. Chem.*, 1918, **104**, 11—47).—A continuation of the work of Hedin and Masai (A., 1918, i, 90). The chief results may be summarised as follows: The serum shows itself either completely inactive or very slightly active towards casein, but undoubtedly capable of breaking down peptone when tested by the tannic acid method. If the serum is fractionated with ammonium sulphate, the globulin fraction, precipitated by about one-third saturation, contains primary and secondary protéases, and thus causes fission of casein and peptone. The first type of activity appears to be lost if the serum is heated at 56° during thirty minutes, whereas the second type persists in a greatly lessened degree. The albumin fraction precipitated between half and full saturation contains practically only secondary proteases, which are active towards peptone but not noticeably towards casein; it contains also substances which inhibit the activity of pancreas trypsin as well as of the primary proteases of the globulin fraction. The power of these inhibiting substances is destroyed or weakened by treating the albumin with chloroform or ether; if, however, they have already acted on the enzyme, subsequent treatment with chloroform is ineffective. H. W.

The Increase in Nitrogen Metabolism of the Dog, following the Administration of Desiccated Thyroid Gland. ALICE ROHDE and MABEL STOCKHOLM (*J. Biol. Chem.*, 1919, **37**, 305—316).—Nitrogen elimination in the dog receiving only sugar solutions may be increased approximately 50% by the administration, during a five- to seven-day period, of commercial desiccated thyroid gland in doses of 0·10—0·15 gram per kilo. of body weight.

W. G.

The Acid-Base Balance in Animal Nutrition. I. The Effect of certain Organic and Mineral Acids on the Growth, Well-being, and Reproduction of Swine. ALVIN R. LAMB and JOHN M. EVVARD (*J. Biol. Chem.*, 1919, **37**, 317—328).—With the view of testing the ability of swine to metabolise successfully the lactic and acetic acids of silage, four lots of two pigs each, all from the same litter, were fed with equal amounts of a good basal ration consisting of ground corn 80%, meat meal tankage 15%, standard wheat middlings 5%. One lot served as a control and the other three received in addition, respectively, sulphuric, lactic, and acetic acids in amounts increasing gradually up to 500 c.c. of *N*-acid per pig per day during 150 days. The three acid-fed lots grew practically as rapidly as the control, and remained in equally good condition. The organic acids seemed to be completely oxidised, and the sulphuric acid was neutralised without apparent harm or significant effect on growth. An examination of the blood at the end of the experiment showed that neither the organic nor mineral acids disturbed the reaction of the blood.

The two pigs fed with sulphuric acid were continued on the same ration for four to six months longer, and successfully produced young, but either the excessive amount of acid fed or some other factor prevented the successful rearing of the young. W. G.

The Acid-Base Balance in Animal Nutrition. II. Metabolism Studies on the Effect of certain Organic and Mineral Acids on Swine. ALVIN R. LAMB and JOHN M. EVVARD (*J. Biol. Chem.*, 1919, **37**, 329—342. Compare preceding abstract).—Metabolism studies on a growing pig fed on a ration containing a liberal allowance of calcium show that the animal apparently oxidised the organic acids (lactic and acetic) completely with no increase in urinary ammonia, and that the acids seemed to bring about a slightly increased retention of calcium. On the same basal ration plus 300 c.c. of *N*-sulphuric acid per day, 61% of the acid ingested was neutralised by means of ammonia, and 4·6% was accounted for by extra urinary acidity. On another basal ration very low in calcium, extra ammonia excretion accounted for 76% of the acid fed, and extra urinary acidity for 10%. On neither ration did the mineral acid cause a significant loss of calcium, nor did it interfere with the storage of protein. W. G.

The Mechanism of the Action of Fats in the Utilisation and Assimilation of Proteins. F. MAIGNON (*Compt. rend.*, 1919, **168**, 474—476. Compare A., 1918, i, 416).—The author con-

siders that the fats exercise a favourable action on the assimilation of albumin by intervening in the synthetic reconstitution of the proteins, and that in this action not only the glycerol portion of the fat molecule exercises an influence as already shown by Maillard, but also the fatty acid portion. Thus the fatty acids may combine with the amino-acid nucleus of a protein in formation and permit of the building up of a molecule, which it would not have been possible to obtain simply with the amino-acids available and without the assistance of the fats. W. G.

A Method of Expressing Numerically the Growth-promoting Value of Proteins. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem.*, 1919, **37**, 223—229).—From feeding experiments with rats in which the proportion of protein in the food was so restricted that the protein factor alone determined the rate of growth, the authors determined, within limits, the concentration which promoted the greatest gain of body weight relative to the protein ingested by supplying foods containing different percentages of protein. The results indicate, in the first place, the necessity for employing a large number of animals. When an animal is restricted to such a quantity of protein that a maximum gain of body weight is made per unit of protein eaten, it grows at less than the normal rate. Economy in nutrition during growth depends on a correct adjustment between the proportion of protein and the total energy supplied, the optimum of protein being determined not only by the absolute amount furnished, but also by its quality. W. G.

Accessary Factors in the Nutrition of the Rat. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, 12. 408—415).—An antiscorbutic does not fulfil the physiological function of the fat-soluble *A* when it replaces it in the diet of the rat. The authors confirm the observation of McCollum and co-workers and of Drummond that by depriving rats of the antineuritic factor a dietetic deficiency is brought about, as a result of which a fatal termination ensues if the diet is not rectified in time. Rats subsisting on a diet containing the antiscorbutic factor as well as the water-soluble and fat-soluble *A* factors grow better than rats from the diet of which the antiscorbutic factor is absent. W. G.

Antiscorbutic Properties of Concentrated Fruit Juices. ARTHUR HARDEN and ROBERT ROBISON (*J. Army Med. Corps*, 1919, **32**, 48—56).—Orange-juice, evaporated at 40° under reduced pressure, gives a solid residue in which the antiscorbutic principle is still largely intact and remains so in a dry atmosphere at the ordinary temperature for six months. Apple jelly prepared in a Kestner evaporator also possesses antiscorbutic properties in a high degree. but is inferior to orange juice. G. B.

Dietary Properties of the Pea (Vicia sativa). E. V. MCCOLLUM, N. SIMMONDS, and H. T. PARSONS (*J. Biol. Chem.*, 1919, **37**, 287—301).—Pea proteins are of very poor quality when

fed as the sole source of nitrogen. Casein and zein supplement the deficiencies of the pea proteins, but gelatin and lactalbumin do not. There is an indication of the presence in peas of some substance or substances which prove injurious when taken in large amounts, but the toxicity, if there be any, is but slight and only manifests itself when diets extremely rich in peas are persisted in over a long period.

From the failure of lactalbumin to supplement the proteins of the pea, or to induce growth when fed in the amounts used in the experiments described, the authors tentatively conclude that lactalbumin is either an incomplete protein or a poorly constituted one.

W. G.

Zinc, a Cellular Constituent of the Animal Organism. Its Presence and Rôle in the Venom of Serpents. C. DELEZENNE (*Ann. Inst. Pasteur*, 1919, **33**, 68—136).—Of the zinc occurring in the blood of animals, the major portion is found in the leucocytes, a little in the red corpuscles, and practically none in the plasma. An examination of the different organs of a number of animals of different species shows that zinc is a constant constituent of all animal cells. In the venom of serpents it is present to the extent of 0·31—0·56% in the venom of Colubrides and 0·11—0·23% in that of Viperides, and is present, combined with organic constituents, in such a manner as not to be precipitated by hydrogen sulphide or separated by dialysis even in the presence of hydrochloric acid. It is probably combined with a proteose rich in sulphur, since the sulphur and zinc contents of the different venoms examined varied very closely in the same direction. The proportion of zinc present in the venoms was found to vary inversely with the proteolytic and coagulating properties of the venoms. On the other hand, the zinc content was found to run parallel with the nucleolytic activity and the diastatic activity, which gives rise to hæmolysis, venoms with high zinc content showing the greatest activity in these two directions. In this connexion it should be noted that in mammals it was found that those organs which were richest in phosphatides and nucleic acids had the highest zinc contents.

W. G.

Behaviour of the Kidneys towards some Isomeric Sugars (Dextrose, Lævulose, Galactose, Mannose, and Sucrose, Maltose, Lactose). H. J. HAMBURGER and R. BRINKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 548—561).—When Ringer's solution containing dextrose is passed through the kidneys (of frogs), this sugar is retained by the glomerulus membrane, whereas lævulose and mannose are allowed to pass entirely and galactose to a large extent. Sucrose, maltose, and lactose also pass through this membrane, the last perfectly; the membrane is also permeable to raffinose.

T. H. P.

The Physicochemical State of the Proteins in Cow's Milk. LEROY S. PALMER and ROBERT G. SCOTT (*J. Biol. Chem.*, 1919, **37**, 271—284).—Samples of fresh skim-milk, skim-milk preserved either with 5% of chloroform or 0·05% of formaldehyde, and of the lactic acid whey from fresh skim-milk were filtered, under pressure, through Pasteur-Chamberland tubes, and in the filtrate the total protein, as precipitated by Almen's tannic acid reagent, and the non-protein nitrogen were determined. The amount of non-casein protein recovered in the filtrate did not in any case exceed 10% of the non-casein protein in the original milk, and in most cases was considerably less than this figure. There was also only a partial recovery of the non-protein nitrogen of the original milk in the experiments with milk preserved with chloroform and formaldehyde. These results differ widely from those of Van Slyke and Bosworth (compare A., 1915, i, 192). The authors consider that it is fallacious to draw conclusions regarding the true state of solution of non-casein proteins of milk based on filtration studies of this character, since there is considerable variation in size of the pores of different Pasteur-Chamberland filters. W. G.

The State of Proteins in Cow's Milk. L. L. VAN SLYKE and A. W. BOSWORTH (*J. Biol. Chem.*, 1919, **37**, 285—286. Compare A., 1915, i, 192).—A reply to Palmer and Scott (compare preceding abstract). W. G.

Creatinuria and Acidosis. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **37**, 245—252).—Feeding experiments carried out with two normal boys, four women suffering from hyperthyroidism, and two normal women did not demonstrate any definite connexion between changes in acid-base equilibrium and creatine excretion. W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Effect of Acids on the Growth of Bacillus coli. FRANK JOHN SADLER WYETH (*Biochem. J.*, 1918, **12**, 382—401).—All strains of *Bacillus coli*, whether of human or bovine origin, behave similarly when exposed to similar conditions. The degree of acidity of the final reaction produced by a culture of *B. coli* cannot be used for diagnostic purposes, the value not being a "physiological constant," but dependent on (*a*) the initial hydrogen-ion concentration of the medium in which fermentation occurs; (*b*) the composition of the medium, especially the degree to which it is "buffered"; (*c*) the nature of the acid used to produce the initial reaction of the medium. When the amount of acid added is insufficient completely to inhibit the fermentation

of *B. coli* therein, a definite latency of growth results, the latency increasing with the amount of acid initially added. Each acid has its own specific effect in inhibiting the growth of *B. coli* in a given medium, the inhibiting effect being greater as the acid is more highly dissociated. For a mixture of any given medium and acid, there appears to be a definite critical point, beyond which the slightest rise in the degree of acidity results in a complete inhibition of the growth of *B. coli*. W. G.

Effect of Carbon Disulphide and Toluene on Nitrogen Fixing and Nitrifying Organisms. P. L. GAINEY (*J. Agric. Res.*, 1918, **15**, 601—614).—Carbon disulphide and toluene, if applied to soils in sufficient quantity, will destroy *Azotobacter* and check the accumulation of nitrates, and possibly will destroy nitrifying organisms. The amounts of these two antiseptics necessary to produce this effect vary widely with the conditions, being affected particularly by the moisture content of the soil, diminishing as the latter increases. Providing that sufficient antiseptic is added to have any effect on *Azotobacter*, they are usually completely destroyed, but, on the other hand, there is a great difference in the amount necessary to destroy nitrifying organisms and that necessary to check their activity. Unless nitrification has been checked, there is no appreciable accumulation of ammonia following the treatment with these antiseptics.

There are nitrogen-fixing organisms other than *Azotobacter* present in soils, which are not destroyed by the addition of 10 c.c. of carbon disulphide or toluene to 100 grams of soil, even when the moisture content of the soil is high. W. G.

Production of Citric Acid by Sterigmatocystis nigra [Aspergillus niger]. MARIN MOLLIARD (*Compt. rend.*, 1919, **168**, 360—363).—In culture solutions containing insufficient quantities of nitrogen and mineral salts for the sugar present, *Aspergillus niger* produces citric rather than oxalic acid, the amount increasing gradually at first, and then considerably between the eighth and tenth days, after which it remains almost constant. Citric acid is noticeable from the very first, but oxalic acid only appears towards the end of the second day, just at the time when the conidiæ commence to be formed, its amount only increasing very slowly. W. G.

Course of the Formation of Diastase by Aspergillus niger. F. A. F. C. WENT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 479—493).—*Aspergillus niger* was grown in the dark at $24 \pm 0{\cdot}5^{\circ}$ in a culture solution containing 5% of dextrose, 0·5% of ammonium nitrate, 0·1% of potassium phosphate, and 0·05% of magnesium sulphate in glass flasks, the amount of diastase present in the liquid and in the fungus mass being determined at first daily and later every two, three, or more days. The method of determination consisted in ascertaining the length of time necessary

for the complete disappearance of the starch from a starch solution of definite strength mixed with the enzyme solution. The tests were made with a solution containing 0·0625 gram of iodine and 0·0625 gram of potassium iodide to 100 grams of water, 1 c.c. of this being found to give a distinct blue coloration with 0·001 gram of soluble starch, or a definite reddish-violet coloration with 0·0002 gram, in 10 c.c. of water.

During the first days after germination of the mould spores with which the culture liquid was inoculated, a great quantity of diastase is formed in the mycelium, this being accompanied by destruction of the enzyme, which is at first negligible in comparison with the formation, but soon makes itself so evident that the total quantity of diastase quickly decreases from the maximum reached about five days after the commencement of germination. Never more than a very small part of the total amount of the enzyme occurring in the mycelium passes into the nutrient solution, this being perhaps derived partly from dead cells. T. H. P.

Occurrence of Iodine in Plants. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1918, **104**, 54—58).—The author has examined a considerable number of plants in respect of iodine content. The method employed consisted in ashing the plant in an alkaline condition and treatment of the residual mixture of salts with 95% alcohol, in which any iodides are soluble. The aqueous solution of the extract was treated with a solution of nitrosylsulphuric acid in concentrated sulphuric acid in the presence of chloroform, in which any liberated iodine dissolved to a red solution. Test experiments showed that 0·04 mg. of added iodine could be detected in 10 grams of spinach by this method.

Minute amounts of iodine are shown to occur in *Beta vulgaris*, *Solanum tuberosum*, *Apium graveolens*, *Lactuca sativa*, and *Daucus carota*. Iodine could not be detected in the fruit, seeds, tubers, or leaves of *Taxas baccata*, *Pinus silvestris*, *P. cembra*, *Abies pectinata*, *Zea Mays*, *Oryza sativa*, *Avena sativa*, *Hordeum sativum*, *Secale cereale*, *Triticum sativum*, *Allium cepa*, *Fagus silvatica*, *Castanea vesca*, *Cannabis sativa*, *Urtica dioica*, *Polygonum fagopyrum*, *Spinacea oleracea*, *Lepidium sativum*, *Ribes grossularia*, *Pirus malus*, *P. communis*, *Prunus cerasus*, *Lupinus albus*, *L. angustifolius*, *Trifolium pratense*, *Vicia sativa*, *Pisum sativum*, *Soja hispida*, *Phaseolus vulgaris*, *Vitis vinifera*, *Stachys tuberifera*, *Curcurbita pepo*, or *Aesculus hippocastanum*, or in the following fungi: *Cantharellus cibarius*, *Boletus edulis*, *Agaricus campestris*.

Iodine could not be detected in eight samples of milk, in five varieties of cheese, or in cow's urine. H. W.

Chemical Composition of Agave americana, L. The Chemistry of Succulent Plants in General. JULIUS ZELLNER (*Zeitsch. physiol. Chem.*, 1918, **104**, 2—10).—The leaves of *Agave americana*, L., have been submitted to chemical examination along

the usual lines. The fresh leaves are remarkable for their high water content. For examination, the air-dried material was taken. The light petroleum extract (1·03%) contained fat, chlorophyll, and wax; the ethereal extract (0·74%) consisted of waxy matter. The aqueous extract (50·75%) was composed of amorphous carbohydrates (12·00%), sugar (calculated as dextrose, 12·68%), malic acid (about 8%), free acid (as H ions, 0·02%), ash (7·54%), other matter, such as small amounts of peptones, amino-acids, etc. (about 10%). The portion insoluble in indifferent solvents contained crude cellulose, including bast fibres (17·85%), pentosans (7·44%), methylpentosans (1·01%), pectin, hemicelluloses, oxalate (about 13%), mineral matter (4·82%), crude protein (3·25%).

The results are compared with those obtained from the examination of other succulent plants so far as the data are available. The high content of water-soluble substance, of calcium malate, of pectinous matter, and probably of sugar appears to be characteristic of the class, but it is not possible at present to decide whether the poverty in nitrogen and iron is a general feature. Further, it would appear that a volatile substance, probably an aldehyde, is frequently present in this class of plant. H. W.

Is Selenium Present in the Vegetable and Animal Organism? R. Fritsch (*Zeitsch. physiol. Chem.*, 1918, **104**, 59—64).—According to Gassmann (A., 1916, i, 772; 1917, ii, 540), selenium is to be regarded as a definite constituent of the human, vegetable, and animal organisms. The author, however, considers that the methods on which Gassmann relies cannot give trustworthy results. He has therefore examined the question further, and has been unable to detect the presence of selenium in thirty-five samples of spinach, clover, corn, potatoes, or bones. The method adopted consisted of ashing the plant in the presence of sodium carbonate and sodium nitrate, and finally obtaining any selenium present as a solution of selenious acid in concentrated sulphuric acid; in this solution, the presence of selenium is detected by the green to bluish-green coloration with codeine, or the intense yellow coloration with colchicine. Test experiments showed that 2—0·5 mg. of selenious acid could be detected in 30—50 grams of plant material in this manner.

Selenium does not appear to be present in urine or bones.

H. W.

The Microchemical Detection and the Distribution of Soluble Oxalates in the Vegetable Kingdom. H. Molisch (*Flora*, 1918, **11—12**, 60—70; from *Physiol. Abstr.*, 1919, **3**, 540).—The methods employed by the author to ascertain the presence of soluble oxalates in plants were precipitation with (1) saturated alcoholic sodium hydroxide; (2) saturated alcoholic potassium hydroxide; (3) lead acetate; (4) barium chloride. Two hundred and forty plant species were examined. Soluble oxalates were found frequently in the phanerogams, and the following families

contained large quantities: Polygonaceæ, Chenopodiaceæ, Amarantaceæ, Aizoaceæ, Begoniaceæ, Milostomaceæ, Oxalideæ, Cannaceæ, and Marantaceæ. W. G.

Spectrographic Study of the Ashes of Marine Plants. EUGÈNE CORNEC (*Compt. rend.*, 1919, **168**, 513—514).—From a spectrographic study of the ashes of *Laminaria*, the presence of the following elements was shown: Group I, silver, arsenic, cobalt, copper, manganese, nickel, lead, and zinc; Group II, bismuth, tin, gallium, molybdenum, and gold; Group III, antimony, germanium, glucinum, titanium, tungsten, and vanadium. The elements of Group I have previously been detected in marine plants, those of Group II in sea-water, whilst those of Group III have not been previously reported as occurring either in sea-water or in marine plants. Gold, bismuth, germanium, and gallium were only present in spectrographic traces in the ashes examined. W. G.

Application of the Biochemical Method to the Study of the Leaves of Hakea laurina. Extraction of a Glucoside (Arbutin) and of Quebrachitol. EM. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1919, **168**, 414—417).—From a study of the rotation of an extract of the leaves of *Hakea laurina*, R. Br., made by alcohol, after subsequent defecation and removal of the alcohol, first directly and then after the action, first, of invertase, and, secondly, of emulsin, the authors show the presence of sucrose, of two glucosides, and of a lævorotatory substance, not hydrolysable by emulsin, in the leaves. By the use of suitable solvents they have isolated quebrachitol and arbutin in their crystalline forms and characterised them. W. G.

Ovalbumin Constitutes a Complete Food for Isaria densa. MARIN MOLLIARD (*Compt. rend.*, 1919, **168**, 523—524).—Ovalbumin, prepared from the commercial material by solution in water and subsequent coagulation by heat in such a manner as to obtain it as a very finely flocculated mass which is filtered off and strongly pressed, satisfies all the nutritive requirements of *Isaria densa*. The phenomena of intense oxidation of ovalbumin give rise to a very low respiratory quotient and the formation of oxalic acid. W. G.

The Microchemical Reactions and Localisation of the Alkaloid of Isopyrum thalictroides, L. MARCEL MIRANDE (*Compt. rend.*, 1919, **168**, 316—317).—The author gives a number of microchemical tests for detecting the presence of the alkaloid, isopyrine, in the plant cells, and shows that it occurs, in the case of *Isopyrum thalictroides*, principally in the subterranean organs, which are at all seasons very rich in the alkaloid and to a less extent in the green aerial organs. [See, further, *J. Soc. Chem. Ind.*, 1919, 197A.] W. G.

General and Physical Chemistry.

Reversal of Spectrum Lines Produced by a Spark under Water. TOSHIKAZU MASHIMO (*Mem. Coll. Sci. Kyoto. Imp. Univ.*, 1918, **3**, 73—79).—The spectra of aluminium, zinc, cadmium, and mercury, produced by sparking between poles of these metals under water, have been examined down to $\lambda = 1850\ \mu\mu$. It is shown that certain of the lines are reversed by this process; in the case of aluminium the lines λλ 1930, 1935, 2205, 2210, 2263, 2268, 2367, 2378, 2567, 2575, 2653, 2661, 3082, 3093, and 3944$\mu\mu$ are reversed. With zinc the lines λλ 2026, 2062, 2087, 2097, 2102, 2105, 2139, 2288, and 2832 (?) suffer reversal. Cadmium gives the lines λλ 2144, 2288, 3069, and 3095 $\mu\mu$ reversed, whilst in the case of mercury the lines λλ 2482 and 2537 $\mu\mu$ are reversed. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Helium. II. TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto. Imp. Univ.*, 1918, **3**, 81—92. Compare A., 1917, ii, 401). —Making use of Lo Surdo's method, the effect of electric fields (3000—70,000 volt per cm.) on the helium lines λλ 4169, 4144, 4026, 4009, 3965, 3868, 3830, 3820, 3614, 3448, and 2945 has been examined and the results compared with those of Stark, Brunetti, and Koch. It is shown that helium lines are effected in three ways by an electric field, (1) symmetrical resolution (λ 4686), (ii) non-symmetrical resolution (diffuse series of lines of helium and parhelium), (iii) one-sided displacement (principal series lines and sharp series lines of helium and parhelium). In the last-named case only the lines belonging to the principal series of parhelium are displaced toward the violet, whilst the other three series lines are displaced toward the red. Diffuse series lines are usually accompanied by an isolated component on the violet side, the starting point of which approaches more nearly to the initial line as the term number increases. The line λ 3830, the position of which was calculated by Koch, but not observed by him, appears in the photographs of some of the present experiments. Two lines, λ 2804 and 2482 Å.U., which are probably due to mercury, were also found to be displaced slightly towards the red in an electric field. J. F. S.

Investigation of Extreme Ultra-violet Spectra, with a Vacuum-grating Spectrograph. J. C. MCLENNAN and R. J. LANG (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 258—273).—A preliminary paper, in which a full description of a vacuum-grating spectrograph designed and made by the Adam Hilger Company is given. The theory of the concave grating is developed, and the experimental details for determining wave-lengths by means of this instrument are described. A short summary of the previous work in the extreme ultra-violet region precedes a description of the various

types of arcs used in the present examination of the extreme ultra-violet spectra of mercury, copper, iron, and carbon. The spectra were photographed on Schumann plates made by Hilger, and the wave-lengths are measured to within one Ångstrom unit. In the case of mercury nine lines appear in the photograph, lying between $\lambda=2054$ Å.U. and $\lambda=1435$ Å.U.; with copper thirteen lines appear between $\lambda=2243$ Å.U. and $\lambda=1925$ Å.U.; in the case of iron twenty-seven lines are found between $\lambda=2027$ Å.U. and $\lambda=1427$ Å.U.; carbon shows twenty-eight lines between $\lambda=2023$ Å.U. and 584 Å.U. Photographs of all the spectra are reproduced in the paper. J. F. S.

Emission and Absorption in the Infra-red Spectra of Mercury, Zinc, and Cadmium. RAYMOND C. DEARLE (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 280—299).—The absorption spectra of mercury, zinc, and cadmium have been measured in the infra-red region; for the region up to 8500 Å. the spectrum was photographed, whilst above this wave-length a linear thermopile and galvanometer were used. The light was obtained from a mercury amalgam lamp of the Heraeus type; the amalgam consisted of 60% mercury, 20% lead, 20% bismuth, ½% zinc, and ½% cadmium. In some cases an arc of the metal in a vacuum was employed. For the energy measurements a 100 volt Nernst glower was used. In the case of mercury absorption bands $\lambda=1\cdot014\,\mu$, $1\cdot038\,\mu$, $1\cdot065\,\mu$, $1\cdot089\,\mu$, $1\cdot129\,\mu$, $1\cdot160\,\mu$, $1\cdot207\,\mu$, and $1\cdot359\,\mu$ were observed. Energy measurements were made in the region $1\cdot2$—$1\cdot5\,\mu$, the only absorption band observed lying at $\lambda=1\cdot359\,\mu$. No absorption was shown in the case of the energy measurements of zinc until the temperature had been raised to 275°. At this temperature absorption was observed at $\lambda=1\cdot105$; in the longer wave-lengths evidence was more difficult to obtain, but indications of absorption were obtained at $\lambda\lambda\,1\cdot379\,\mu$, $1\cdot41\,\mu$, $1\cdot57\,\mu$, and $1\cdot65\,\mu$. With cadmium vapour absorption was found at $\lambda=1\cdot040\,\mu$, which is the first line of the series $\nu=(2\cdot5S)-(m,P)$; a second strong absorption band occurs at $\lambda=1\cdot503\,\mu$, whilst less marked absorption occurs at $\lambda\lambda=1\cdot129\,\mu$, $1\cdot395\,\mu$, $1\cdot4475\,\mu$, $1\cdot522\,\mu$, and $1\cdot563\,\mu$. By the photographic method a line was observed at $6977\cdot4$ Å. in one series of experiments, but this line could not be reproduced. Some absorption experiments were carried out with a quartz cell containing cadmium iodide; it was found that there was no absorption in the visible and ultra-violet regions at comparatively low temperatures, but with increased temperature a broad band was observed which extended from the limit of the ultra-violet end of the spectrum up to a wave-length of about $\lambda=4000$ Å. Attempts to resolve this band failed. In the longer wave-lengths no absorption was visible at wave-lengths characteristic of the cadmium spectrum. Energy measurements made in the long wave-length region above $\lambda=1\cdot0\,\mu$ showed the presence of an absorption band at $\lambda=1\cdot040$ when the temperature of the cell was above that necessary for dissociation. The emission and absorption curves obtained by bombarding mercury vapour

with electrons with the object of producing the single line spectra are given. J. F. S.

Characteristic Ultra-red Vibrations of Diatomic Crystals. M. BORN (*Physikal. Zeitsch.*, 1918, **19**, 539—548).—A mathematical paper; in which the relationship between the constants of a diatomic regular crystal grating is considered. The influence of electrons on the index of refraction in the ultra-red is also considered mathematically. The results obtained are applied to crystals of rock salt, sylvine, potassium bromide, potassium iodide, pyrites, fluorspar, and sodium chlorate. J. F. S.

Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium. J. C. MCLENNAN and J. F. T. YOUNG (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 273—279).—The absorption spectra of calcium, strontium, and barium have been determined, and from the values of the wave-lengths the ionisation potential of these elements calculated. In the case of calcium a hollow carbon filled with metallic calcium was used, and it was observed that the reversals were confined entirely to those wave-lengths which were members of the series $\nu=(1{\cdot}5,S)-(m,P)$; as given by Lorenser (Inaug. Diss.) these are:

m =	2.	3.	4.	5.	6.	7.
λ =	4226·91	2721·77	3298·66	2275·60	2200·8	2151·00

m =	8.	9.	10.	11.
λ =	2118·99	2097·8	2083·2	2072·8

In the case of strontium the sulphide was employed instead of the metal, and the wave-lengths for $\nu=(1{\cdot}5,S)-(m,P)$ also accord with those of Lorenser. The following were found:

m =	2.	3.	4.	5.	6.
λ =	4607·52	2931·98	2569·60	2428·16	2354·40

m =	7.	8.	9.	10.	11.
λ =	2307·5	2275·5	2253·5	2237·4	2226·0

In the case of barium the oxide was used, and by noting the reversals nine members of the series $\nu=(1{\cdot}5S)-(m,P)$ were obtained; these are:

m =	2.	3.	4.	5.	6.
λ =	5535	3275	2845	2597	2542
ν =	10864·6	30534·4	35149·4	38502·1	39339·1

m =	7.	8.	9.	10.
λ =	2498	2470	2455	2441
ν =	40032	40486	40733·2	40966·8

From the limiting frequencies of the single series of the spectra the following ionisation potentials of the vapours have been calculated: mercury, 10·45 volts; zinc, 9·4 volts; cadmium, 9·0 volts; magnesium, 7·65 volts; calcium, 6·12 volts; strontium, 5·7 volts; and barium, 5·21 volts. J. F. S.

Changes in Spectrum Intensity and Weakening of the Iodine Fluorescence by means of a Magnetic Field. W. STEUBING (*Ann. Physik*, 1919, [iv], **58**, 55—104).—In a previous note (*Verh. deut. physikal. Ges.*, 1913, 1181) it was shown that when fluorescent iodine vapour is brought between the poles of a powerful electric magnet, the intensity of the fluorescent light is greatly diminished. The present paper deals with the investigation of this phenomenon. The light changes have been investigated spectrophotometrically and spectrographically, and a series of energy measurements have also been made. It is shown that it has been impossible to attribute the weakening of the iodine fluorescence to any definite cause, but that it depends on the action of a magnetic field on the electron vibrations which give rise to the emission of a band spectrum. The effect is greater with the higher frequencies than with the lower, and, further, the magnetic field has a more pronounced action the greater the vibration amplitude during the emission. The present phenomenon, therefore, has nothing in common with other processes which diminish or destroy fluorescence. The magnetic action has little to do with the actual fluorescence, and the same effect is to be expected if the same band spectrum is produced in some other way; it is to be expected that the magnetic weakening will take place more easily the greater the energy per molecule with which the emission occurs, and consequently an electrically produced spectrum will be correspondingly more strongly weakened by weaker magnetic fields. J. F. S.

The Magnetic Field and the High Frequency Spectrum of the Elements. RITA BRUNETTI (*Nuovo Cim.*, 1918, [vi], 16, ii, 5—18).—Assuming that the action of a magnetic field results in decomposition of high frequency radiations, the results of the author's experiments show that the ordinary means of spectral analysis would be insufficient to reveal directly such decomposition if the latter were of the type and order of magnitude of the Zeeman phenomenon. None of the theories on the emission of high frequency radiations excludes the possibility of a decomposition produced in this manner. The lines of the *K* spectrum for iron, nickel and copper are found by the curved crystal method to be double, the mean difference between the two components being 8/1000 and 11/1000 Ångström units for the α and β lines respectively. No qualitative modification of any kind is exhibited in the characteristic spectra of these elements under the influence of magnetic fields of moderate magnitude and degree of variation. T. H. P.

Light Positive and Light Negative Photophoresis [in Connexion with] Sulphur and Selenium. IRENE PARANKIEWICZ (*Ann. Physik*, 1918, [iv], **57**, 489—518).—It has been shown by Ehrenhaft (*ibid.*, 1918, **56**, 81) that particles of matter fall under the action of gravity, but rise, in an electric field; some particles when subjected to a strong beam of light are deflected, in the horizontal direction, from their original path. Thus sulphur particles

move in the direction opposite to that of the beam of light (light negative); selenium particles under some conditions move in the direction of the beam of light (light positive). The present paper is a continuation of this work, and deals with the dependence of the photophoresis on the chemical nature of the particles, the intensity of the light, pressure of the surrounding medium, and the size of the particles. The work has been carried out with sulphur and selenium particles of radius $8-60\times10^{-6}$ cm. The methods adopted in the investigation were similar to those employed by Ehrenhaft. It is shown that sulphur particles are always light negative, whereas selenium particles are either light negative or light positive, depending on the duration of heating in the production of the particles. The light negative photophoric force on selenium particles is approximately six times as great as the force of the same light beam on sulphur particles of the same mobility. The intensity, with which particles of a given material react on the light, is dependent on the size of the particles. The negative photophoresis shows its maximum action on sulphur particles of radius 27×10^{-6} cm., and on selenium particles of radius 15×10^{-6} cm. The photophoric force on sulphur and negative selenium is independent of the time, whilst with positive selenium it is a function of the time. The power of reaction on the light of positive selenium decreases with time. The photophoric force is independent of the surrounding gas and also of the pressure. The independence of the photophoric force on the pressure, the chemical nature of the surrounding gas, the decrease of the positive reaction of selenium particles which is due to an internal change of the selenium, and, further, the fact that particles of different materials, but of the same mobility, are very differently acted on by light, all tend to confirm the conclusion of Ehrenhaft that the action is a direct one of the light on the material. J. F. S.

X-Ray Spectra and the Constitution of the Atom. II. L. VEGARD (*Phil. Mag.*, 1919, [vi], **37**, 237—280. Compare A., 1918, ii, 144).—A theoretical paper, in which the process of recombination of the primaries is discussed, together with some of the consequences which follow from them. Calculations are made of the quant-number and the number of electrons of the ring systems from the observed frequencies. The possibility of there being two L and two M rings is considered. It is shown that whether recombination is assumed from a normal or deformed primary system, or recombination from a secondary one, it must be assumed that the angular momentum of the electrons left behind in the atom remains unchanged; and further it must be assumed that the changes of energy of the systems situated between the broken ring and the ring of departure enter into the energy quantum of radiation which is emitted as the result of recombination. On the basis of the theory of the production of X-rays developed by the author it must follow that recombination takes place from secondary systems, and that always the angular momentum of the electrons left behind

in the atom is kept constant during expulsion and recombination. A number of relationships of the atomic constitution and properties of the atoms are given. All elements belonging to the same period of the periodic classification have the same quant-number, and this number increases by one unit on passing from one period to the next. J. F. S.

Radioactivity and the Coloration of Minerals. EDGAR NEWBERY and HARTLEY LUPTON (*Mem. Manchester Phil. Soc.*, 1918, **62**, No. 10, 1—15).—The colours obtained on exposing various substances to the action of the β- and γ-rays of radium, and sometimes to the α-, β-, and γ-rays of the radium emanation, are recorded. Various differently coloured fluorspars, owing to their wonderful range of colours and remarkable thermo-luminescence, proved the most interesting, the changes produced by radium being so varied as to be bewildering. A colourless Matlock fluorspar after twenty-four hours' exposure to 50 mg. of radium became blue, deeper than a copper sulphate crystal, the colour being permanent in the dark but destroyed by direct sunlight, or, more slowly, by daylight and by gentle heating, but the fluorspar may be recoloured by radium indefinitely. Under cathode rays, only a faint purple surface colour was produced. The blue colour is probably due to the γ-rays, as it penetrates right through the crystal. The thermo-luminescence was green and feeble, but a Pyrenean fluorspar, not coloured by radium, gave a remarkable and lasting green light on heating, even though only exposed 150 mm. away from the radium. The thermo-luminescence of Cornish chlorophane is to be ascribed to γ-rays from radioactive materials. On crystal quartz there was no sign of the "rotting" produced by radium rays in fused quartz. The natural colours are discharged by heating, but may be restored by radium.

Clear selenite crystals were coloured brown in regular figures, the remaining parts being colourless, a phenomenon which Miers explains by certain faces of the crystal during growth attracting impurities, to which the colour is to be ascribed. Among other substances examined were diamond, native sulphur, cryolite, rock-salt, sylvine, ruby, anhydrite, celestine, barytes, anglesite, apatite, phosphorite, topaz, zircon, beryl, kunzite, calcite, glass, and bakelite, an artificial amber-like material used for electric insulation. The view that the colours are due to dissociation of minute traces of impurities and the luminescence to the recombination of the products of dissociation is favoured. F. S.

Dependence on Temperature of the Dielectric Constant of some Gases and Vapours. MARIO JONA (*Physikal Zeitsch.*, 1919, **20**, 14—21).—The dielectric constant of air, carbon dioxide, ammonia, sulphur dioxide, methyl alcohol vapour, and steam has been measured at a series of temperatures from 17·8° to 178·1°. Curves of the variation of the constant with temperature are given, and the significance of the curves is discussed mathematically. J. F. S.

Significance of the Volta Effect in Measurements of Electromotive Equilibria. A. SMITS and J. M. BIJVOET (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 562—569).—Application of the more recent views of electromotive equilibria to the Volta effect leads to the result that, on polarisation and passivation, the change in this effect must be great, and that in these phenomena the Volta effect would constitute even the greatest part of the total change in the electromotive force. It is found, further, that if the Volta effect between metals in which the state of internal equilibrium prevails are really very small, as is rendered probable by recent experimental work, this must be regarded as a characteristic property for metals in internal equilibrium.

The values found on measurement of potential differences for metal–electrolyte, termed experimental electrical potentials, always contain an unknown Volta effect, and it is this which renders impossible calculation from the said potentials of the saturation concentrations of the metal ions.

Relations have been derived which contain the solubility product of the metal, the solubility quotient of the non-metal, or the electron concentration in the electrolyte, but not the Volta effect, and these permit of the preparation of a solubility product series of metals and a solubility quotient series of non-metals, from which conclusions may be drawn as to the chemical and electrochemical behaviour of the metals. T. H. P.

Hydrogen Overvoltage. DUNCAN A. MACINNES and LEON ADLER (*J. Amer. Chem. Soc.*, 1919, **41**, 194—207).—None of the theories advanced to account for overvoltage, with the exception of that of Möller (A., 1909, ii, 114), attempts to explain the great influence exerted by the physical condition of the electrode on the overvoltage, a polished platinum electrode, for instance, showing an overvoltage as high as 0·1 volt, whereas that for platinised platinum is nearly zero. The authors have made a number of measurements of hydrogen overvoltage with platinised platinum electrodes, use being made of an apparatus resembling, but differing in detail from, that of Thiel and Breuning (*Zeitsch. anorg. Chem.*, 1913, **83**, 329). With such low currents that one bubble of hydrogen appears in one or more minutes, fluctuations in the overvoltage are observed, the curve connecting overvoltage with time being sinuous with a sharp break invariably following the highest voltage. At low current densities, the bubbles come off at one point and continue to do so, no matter how long the observations are continued, so that each bubble probably leaves a nucleus behind it when it becomes detached.

In explanation of these results, it is assumed that molecular hydrogen, when formed from hydrogen ions by the reaction $2H^+ + 2\epsilon = H_2$, goes directly into solution in the electrolyte immediately surrounding the electrode, so that the hydrogen at that point will tend to rise in concentration and produce a supersaturated solution unless carried away by diffusion, stirring, or other means. If,

however, a nucleus of gaseous hydrogen is present in the electrode, a portion of the hydrogen will enter this gaseous phase, either directly from the electrode or by absorption from the electrolyte, the gaseous nucleus thus playing a part similar to that of a small crystal in a supersaturated salt solution. Hydrogen gas in the form of small bubbles must have a higher energy content per mol. of gas than the same volume of undispersed gas, as energy must be expended in overcoming the surface tension in the formation of small bubbles. Such bubbles will be more soluble, that is, will remain in equilibrium with more concentrated dissolved hydrogen, than the undispersed gas, this phenomenon being analogous to the increase in solubility produced by the fine grinding of solids. Since, other factors being constant, the potential at a hydrogen electrode depends primarily on the concentration of the dissolved hydrogen, an electrode in equilibrium with the small bubbles will reach a higher potential than a similar electrode in equilibrium with the undispersed gas. As electrolysis proceeds and the nucleus of gaseous hydrogen grows, the energy necessary to produce further growth must decrease, since the value of the ratio, increase in surface: increase in volume, is continually decreasing; if the bubble grows slowly, the hydrogen-bearing solution surrounding the electrode will tend to get into equilibrium with the bubble. This accounts for the decrease in overvoltage from a maximum point of the sinuous curve to a minimum point, where the buoyant effect of the solution is sufficient to overcome the attraction of the electrode for the bubble, which breaks away, leaving a nucleus behind. On the rising part of the curve, the concentration of the dissolved hydrogen is increasing to a value such that the nucleus can again grow, and so on. As the bubbles are not always evolved at the minimum points of the curve, it seems probable that, since the nuclei tend to form in depressions in the electrode, the bubbles that separate from the nuclei remain in these depressions until forced out by the growth of succeeding bubbles.

If the electrode can adsorb large hydrogen gas nuclei to start bubble formation, the supersaturation cannot rise to high values and the electrode will have a low overvoltage; metals with small adsorptive powers, however, hold small nuclei and have high overvoltages.

Support of the above explanation is furnished by microscopic examination of various electrodes when evolving hydrogen, this indicating experimental agreement with a theoretical quantitative relation between the size of the bubbles from, and the overvoltage of, platinised platinum electrodes. Further, theory indicates that the overvoltage should increase as the pressure decreases, and this is shown to be the case by the authors' results and also by unpublished work of H. M. Goodwin and L. A. Wilson. T. H. P.

The Modality of Reactions and Chemical Dynamics; Application to the Phenomena of Electrolysis and Spectroscopy. J. MEUNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 49—68).—The

chemical dynamics are the same, in principle, in the different forms of electric cells, which only differ amongst themselves in their complex and variable, secondary reactions. There is the same analogy in the production of spectral rays. The appearance of rays in the spectrum does not characterise, as is usually stated, an element, but rather a reaction of this element, and consequently indicates the presence of another element reacting with it. W. G.

Theory of Specific Heat. II. WALTER JANKOWSKY (*Zeitsch. Elektrochem.*, 1919, **25**, 1—3. Compare A., 1918, ii, 59).—The author answers the criticism of Drucker (A., 1918, ii, 216) made in connexion with the earlier paper, and a further development of the theory of specific heat is contributed. It is shown that the statement that the change of the specific heat with temperature disproves the law of Dulong, Petit, and Joule is incorrect, for in every case regular relationships exist between the specific heat, the number of atoms, and the molecular weight. J. F. S.

Specific Heat Determinations at Higher Temperatures. WALTER P. WHITE (*Amer. J. Sci.*, 1919, [iv], **47**, 44—59).—In determining the specific heats of various substances at temperatures up to 1400° by the method of mixtures, the errors in the final result frequently approach one part per thousand even with precise work. The chief sources of error are: (1) the determination of temperature in the furnace, (2) the loss of heat during the dropping of the charge, (3) the exposure of the calorimeter to the atmosphere during the drop, (4) the effect of external conditions on the calorimeter, and (5) internal effects, such as auxiliary changes in the interior of the calorimeter after the drop.

Of these errors, the variability of the heat losses attending the dropping of the hot substance into the water is surprisingly great and should be prevented.

Modifications in furnaces and in methods of transference to the calorimeter are described in detail. [See, further, *J. Soc. Chem. Ind.*, 1919, 158A.] A. B. S.

Specific Heats of Silicates. II. WALTER P. WHITE (*Amer. J. Sci.*, 1919, [iv], **47**, 1—43. Compare A., 1909, ii, 966).—The specific heats of various silicates at various temperature intervals from 0—1400° were determined, using the method of mixtures, with greater precision than hitherto.

For quartz and silica glass, the values of the interval specific heats satisfy the expressions:

Quartz	$0{\cdot}1685 + 0{\cdot}000194\theta - 0{\cdot}00000011\theta^2$
Silica glass.........	$0{\cdot}1670 + 0{\cdot}000189\theta - 0{\cdot}000000125\theta^2$

The "instantaneous," or true atomic heats, rise regularly from about 3·5 at 0° to about 5·96 (with anorthite to 6·6) at 1300°, the value given by the classical kinetic theory.

The variations of the atomic heat from the theoretical constant

are due partly to secondary thermal effects connected with expansion, change of state or chemical action, and partly to the universal tendency towards a maximum value at a high temperature. The location of the development curve agrees approximately with the values of the atomic vibration frequency, calculated from the known properties of the atoms.

The difference in the value of the elements and compounds shows that it is not a property of the atom, but appears to be related to the combined oxygen.

The calculated specific heat of silica glass at constant volume and that at constant pressure are equal, but the actual heat-temperature curve of silica glass above 600° is above the theoretical value; that of the cristobalite is identical with the theoretical curve at 900°, but then rises above it. With albite and microcline, the specific heat at constant pressure is considerably above the specific heat at constant volume, and this confirms the evidence that the theoretical value of the dimension constant A in the expression $C_p^{3}-C_v=[A(3a)^2\Theta]/Kd$ is exceeded at high temperatures.

On comparing the specific heats of various silicates in the crystalline and glassy form, respectively, it was found that the specific heat of the glass is seldom greater than that of the crystal.

A. Smits' attempts to correlate inversion with equilibrium-temperature changes in liquids or liquid and solid systems have been examined with negative results, and it is suggested that premature fusion due to impurities and sluggishness of transformation account for the observed phenomena.

The conclusion is drawn, from the expansion and specific heats of solids being much less anomalous and irregular than those of liquids, that the molecular changes in solids are of a different order of magnitude. The author partly agrees with Bridgman that there is no relation between the volume, specific heat, and cohesion of pre-inverted and inverted substances, but considers that the change of properties during inversion, although rapidly accelerated at times, is nowhere sudden and discontinuous.

The observed difference in the atomic heat of different crystalline forms of the same substance is so irregular that similar differences with substances of unlike composition must be interpreted cautiously. [See, further, *J. Soc. Chem. Ind.*, 1919, 140A.]

A. B. S.

Specific Heat of Aqueous Solutions with Special Reference to Sodium and Potassium Chlorides. W. R. BOUSFIELD and C. ELSPETH BOUSFIELD (*Phil. Trans.*, 1919, [*A*], **218**, 119—156).—The specific heat of aqueous solutions of sodium chloride and potassium chloride of various concentrations has been determined by the same method and using the apparatus previously described (A., 1911, ii, 580). In each case, the mean specific heat over the temperature ranges 0—13°, 13—26°, and 26—39° was determined. The results of the present work indicate that the specific heat and

specific volume of the combined water may be treated as approximately constant, and the lowering of the specific heat and specific volume of the free water on the introduction of a solute are each proportional to the percentage concentration of the solute. In dilute solutions, the specific heat curve approximates to that of water, which has a minimum at about 25°. In concentrated solutions, the variation of the specific heat with temperature appears to follow an almost straight line law. This behaviour is attributed to the simplification of the water by a considerable destruction of ice and steam molecules, and is analogous to the corresponding phenomenon noted previously (Bousfield and Lowry, A., 1905, ii, 135). The relationship $(dQ/d\theta)_H = L(d\chi/dH)_Q$ is found between the heat of dilution and the contraction. The following constants have been derived: (i) for potassium chloride: the specific heat of the liquid solute, 1·655; the molecular heat of the liquid solute, 123·4; (ii) for sodium chloride: specific heat of the liquid solute, 2·433, and the molecular heat of the liquid solute, 142·1. The number of molecules of water combined with a molecule of solute is calculated for various dilutions. J. F. S.

Neumann-Kopp's Law. FRIEDRICH BÜRKI (*Helv. Chim. Acta*, 1919, **2**, 27—38).—For a number of the elements, the difference, $C_p - C_v$, between the atomic heats at constant pressure and at constant volume has been calculated by means of the formula $C_p - C_v = Ta^2V/41{\cdot}89x$ cal., where V is the atomic volume, a the coefficient of cubical expansion, and x the coefficient of compressibility; for chemically related elements, the differences are, as a first approximation, the same.

In the case of the haloids of the elements of the first group of the periodic table, the Neumann-Kopp law is more exactly fulfilled for molecular heats at constant pressure than for molecular heats at constant volume. C. S.

Determination of Melting Points by means of Electric Heating. SIEGFRIED LAURENS MALOWAN (*Zeitsch. angew. Chem.*, 1919, **32**, i, 16).—Two test-tubes are fastened concentrically one inside the other, leaving a small air-space at the sides and 15 mm. between the bottoms of the tubes. The inner tube is provided with a two-holed rubber stopper, one hole for the thermometer, the other for slipping in the melting-point tube. For making a melting-point determination, the apparatus is fixed with the bottom of the outer tube 5 mm. inside the mouth of a small electrically heated Heraeus crucible furnace. It is claimed that the temperature control is better and the results more accurate than with the usual forms of melting-point apparatus, and, in addition, the whole apparatus can be very quickly cooled. E. H. R.

Boundaries of Existence of the Liquid State. G. BRUNI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 394—397).—The author criticises the conclusions drawn by Herz (A., 1918, ii, 150), who, like Meyer (A., 1918, ii, 292), has overlooked the fact that the true

melting point (triple point, solid–liquid–vapour) does not delimit the liquid state at its lower boundary, the melting point varying with the pressure. Herz considered only twenty-two out of eighty-eight elements, and his deductions have neither theoretical bearing nor empirical confirmation. T. H. P.

Application to Eight Different Substances of the Formula which Expresses the Heat of Vaporisation of a Liquid. E. Ariès (*Compt. rend.*, 1919, **168**, 444—447).—Using the formula previously given (compare *ibid.*, 204), the author has calculated the heat of vaporisation for carbon dioxide, ammonia, stannic chloride, methyl formate, pentane, hexane, heptane, and octane, and finds that the calculated results agree very well with those obtained by different workers. W. G.

Limits of Separation by Fractional Distillation: A New Still-head. S. F. Dufton (*J. Soc. Chem. Ind.*, 1919, **38**, 45—46T). —The still-head described consists of an open tube inside which is another, closed, one with a wire wound spirally round it so that it just fits the outer tube. The latter may be made of parts of different sections increasing in diameter downwards, this gradation of the annulus serving to carry away the increasing volume of condensed liquid; a form more easily constructed consists of one length of tubing of approximately uniform bore, the spirals being wound on cores of decreasing diameter. For any particular set of conditions, there is a certain minimal value for the working volume of the still-head; if this is exceeded, there is no consequent increase in the amount of inseparable mixture in the still-head, the extra length at the bottom becoming filled with vapour and liquid of one of the pure constituents. Such still-heads are far more efficient than the Young pear-bulb column in common use, and have the great practical advantage that the distillation, having been started at the proper rate, slows down and stops when the limit of each pure constituent is reached, rise in the temperature being then necessary to drive off the next constituent. From a mixture of 5 c.c. of benzene with 10 c.c. of toluene, 4·6 c.c. of benzene and 9·4 c.c. of toluene were recovered by direct distillation; the loss was 0·3 c.c. and the unseparated intermediate portion 0·7 c.c., which is not far removed from the actual working volume, the total volume found in the flask at the end of the operation being just twice this amount.

A similar arrangement provides a very efficient means of washing a gas with a small quantity of liquid. In this case, the annulus is made of the same size throughout, and the pitch of the wire spiral is kept as small as practicable so as to reduce the speed of descent of the liquid. Such a washer gives more intimate average contact between gas and liquid and introduces no hydrostatic pressure. T. H. P.

Ultramicroscopic Examination of very thin Deposits, of Metals and Salts, obtained by Evaporation in High Vacua. L. Hamburger (*Kolloid Zeitsch.*, 1918, **23**, 177—199).—The thin

deposits produced on the walls of a vessel in which metals and other substances have been strongly heated have been examined by means of an ultramicroscope. The metals were mounted in the form of thin wires and heated electrically in a vacuum; salts, such as sodium chloride and calcium fluoride, were heated on a tungsten wire. It was found that on admitting air to the cooled vessel, changes in the nature of the film occurred, and in consequence the film was protected by a thin layer of Canada balsam before air was admitted and the ultramicroscopic examination made. The experiments were carried out with the metals silver, gold, tungsten, molybdenum, platinum, iron, copper, nickel, magnesium, zinc, and cadmium, and also with carbon, sodium chloride, and calcium fluoride. It is shown that the metals with high melting points, molybdenum, platinum, nickel, and iron, and also carbon, produce sublimates which are either completely unresolvable or mainly unresolvable into particles. The lower melting elements with a higher vapour tension, gold, silver, copper, magnesium, zinc, and cadmium, show a greater tendency to a less disperse condensation and produce a complete network of ultramicrons. Generally, it can be stated that the higher the temperature necessary for slow sublimation the finer is the structure of the sublimate. The electrical conductivity of films of gold, silver, platinum, and tungsten of measured thickness has also been determined, and it is shown that a covering of calcium fluoride or Canada balsam is a very efficient protection for these metals. Films condensed at the temperature of liquid air, on warming to the ordinary temperature, undergo a non-reversible change of resistance, which is very great in the case of gold and silver. This is probably due to a change in the structure of the deposit, for ultramicroscopically the deposits are seen to be different at the two temperatures. Many deposits undergo a change of resistance when there is no temperature change. In particular, silver deposits produced and kept at the ordinary temperature for long periods increase in their resistance to an infinitely large value. This must be due to changes in the optically unresolvable part of the deposit which lies between the network. These changes are probably of such a nature that small gaps occur, and consequently the direct metallic contact is broken. The influence of the temperature of the walls on which the deposit is formed has been investigated, and it is shown that the higher the vapour tension of the metal is at the temperature of the walls, the less disperse is the structure of the deposit. Many of the metals produce films of definite colours which are characteristic of the metal and are determined by the selective absorption of light by the atoms. J. F. S.

Evaporation and Condensation Velocities and the Calculation of Chemical Constants from the Density of the Condensate. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1919, **105**, 97—111).—A mathematical discussion of the equilibrium between vapour and liquid treated as a simple chemical reaction. From the

gas theory and the thermodynamic laws, formulæ are developed expressing evaporation and condensation velocities in terms of heat of evaporation, molecular heat, molecular weight, molecular diameter, density of the condensate, and closeness of packing. The chemical constant of the "reaction" is the logarithm of the ratio of the maximum evaporation and condensation velocities. It increases with increasing molecular diameter, with decreasing molecular volume, and with decreasing density of packing of the molecules. With increasing molecular weight the constant first rises and subsequently falls continuously. It is shown that all the factors involved in the calculation of the evaporation and condensation velocities can be given a purely mechanical interpretation, with the exception of the heat of evaporation. For the first time a purely mechanical interpretation of the chemical constant is given, its calculation requiring only the molecular diameter, molecular weight, and density.

The method of investigation here used, involving a mathematical analysis of the processes occurring at the surface between two phases, is applicable to other problems, such as the solution of gases in liquids and diffusion problems. E. H. R.

The Extension of the Gas Laws to Liquids and Solids. JOHN SCOTT HALDANE (*Biochem. J.*, 1918, **12**, 464—498).—The three gas laws may be combined and more correctly stated, and at the same time extended to liquids, in the form: The intermolecular volume of a given volume of gas or liquid varies inversely as its mean intermolecular pressure, and directly as the absolute temperature, the concentration of gram-molecules, and a constant which is the same for all gases and liquids. This may be embodied in the equation $P(V-v)=22{\cdot}4nT/273$ or $P(V-v)=0{\cdot}082nT$, where P=mean intermolecular pressure in atmospheres, V=volume in litres, v=volume virtually occupied by the molecules themselves, n=relative number of molecules, so that when P and $n=1$ and $T=273^{\circ}$ absol., $P(V-v)=22{\cdot}4$. This casts new light on the physical properties of solutions and on various phenomena connected with gases and liquids. Thus it can be shown that: (*a*) Diffusion pressure of any one substance between one liquid or gas and another is proportional to the values of its partial pressures p in the one liquid or gas, and $1-v$ in the other. (*b*) The intermolecular pressure is the same for all solutions in the same solvent, up to high concentrations and with wide variations of temperature. (*c*) Osmotic pressure is simply the increased intermolecular pressure required to neutralise the excess of diffusion pressure of a pure solvent inwards over that of a diluted solvent outwards, through a membrane permeable to the solvent, but not to the solute which dilutes it. This excess is given by the equation

$$p_0=0{\cdot}082NT(n/N_1-n),$$

where p_0=osmotic pressure and n, N, N_1=gram-mols. of solute, pure solvent, and solution per litre. (*d*) Diminution of vapour pressure of the solvent and rise of vapour pressure of the solute are propor-

tional to n/N_1. (*e*) Elevation of b. p., and depression of m. p., of the solvent are proportional to $n/(N_1-n)$, and can be calculated respectively if the latent heats of boiling or melting of solvent are known. (*f*) When the ratio n/N_1 is the same in different solutions with the same solvent, the substances, of which n denotes gram-mols. per litre (including the solvent), are in diffusion equilibrium, and their mutual diffusion pressure is $0{\cdot}082NT(n/N_1)$. This diffusion pressure, which has, hitherto, often been confused with osmotic pressure, is of fundamental importance in physical chemistry and physiology. W. G.

The Dissociation Pressures of some Nitrides. ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON (T., 1919, **115**, 215—216).

Structure of Crystals in very thin Laminæ. New Experimental Determination of Molecular Dimensions. RENÉ MARCELIN (*Ann. Physique*, 1918, [ix], **10**, 189—194).—The method employed in the investigation consists in examining a thin sheet of the substance between crossed nicols side by side with a thin wedge of quartz which is moved until the same colour is obtained with both, and from the indices of refraction of the quartz and the thickness of the wedge at the measured point calculating the thickness of the lamina of substance under investigation. By this method laminæ of mica and *p*-toluidine have been examined, and it is shown that with mica laminæ may be obtained of thickness equal to the diameter of the molecules. With *p*-toluidine laminæ have been obtained which are certainly not thicker than twice the molecular diameter and probably not thicker than a single molecular diameter. J. F. S.

The Theory of Gels. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1918, **12**, 351—381. Compare A., 1917, ii, 366).—The low diffusion constant of the natural emulsoids, by retarding the crystallisation of the hot sols, allows the accumulation of a large excess concentration, which, together with their large value of K in von Weimarn's formula, causes gelation on cooling. The small crystallisation velocity is also responsible for the permanency of the gels and the hysteresis of the sols. The viscosity changes in the sols of the natural emulsoids, by heating, are seen to be in conformity with Einstein's formula, since thermal changes cause alterations in the numbers, as well as the size, of the crystallisation centres. Applying von Weimarn's theory to the reversible sol-gel transformation, the conclusion is drawn that gels should comprise two phases, namely, an ultramicroscopic solid phase, bathed in a liquid dispersion medium, from which it has crystallised and which it retains partly by molecular and partly by capillary forces.

Complex organic substances and such as are highly aggregated in solution tend to crystallise as spherites, and this leads to the supposition that the ultimate solid particles of gels are spherites. This

is supported by the fact that by suitable precipitation with alcohol gelatin can be made to assume the form of microscopic spheres.

The liquid adsorbed at the liquid–solid boundary surfaces of gels is under an internal pressure intermediate between those of the solid and of the liquid. This intermediate value of the internal pressure is much greater than that of the free liquid and conditions certain peculiarities in the properties of gels. W. G.

Velocity of Coagulation. H. R. KRUYT and A. E. VAN ARKEL (*Chem. Weekblad*, 1919, **16**, 220—225).—A preliminary note on the measurement of the velocity of coagulation of colloidal solutions. The hydrosol studied is that of selenium prepared by the reduction of selenious acid by means of hydrazine. The concentration of the hydrosol was determined by direct enumeration of the particles under the ultramicroscope, the progress of the coagulation being exhibited by the fall in concentration observed from time to time over a period of thirteen days after the addition of the electrolyte. In presence of potassium chloride solutions of concentration 10 and 20 mg. mol. per litre coagulation of the standard sol was scarcely perceptible; with 40 and 50 mg. per litre coagulation was extremely rapid. The concentration 30 mg. per litre brought about coagulation at a convenient measurable rate. W. S. M.

Forms assumed by Drops and Vortices of a Gelatinising Liquid in Various Coagulating Solutions. EMIL HATSCHEK (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 303—316).—The effect of allowing a 14% gelatin sol to fall drop by drop into a solution of aluminium sulphate or ferrous sulphate is described, and illustrations of the forms assumed by the gelatin drops are given in the paper. Temperature and the density of the coagulating medium determine to a large extent the form assumed. By dropping a solution containing 10 grams of gelatin and 8 grams of crystallised potassium ferrocyanide into a solution of copper sulphate of suitable density, discs were produced which bear a remarkable resemblance to highly magnified blood corpuscles. The effect of the addition of a large number of substances to the gelatin solution is also described.
J. F. S.

Investigations dealing with the State of Aggregation. IV. The Flocculation of Colloids with Salts containing Univalent Organic Ions. S. B. SCHRYVER and NITA E. SPEER (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 400—414).—If adsorption of the discharging ion plays the chief part in the flocculation of colloids, it might be expected that those salts the normal solutions of which have the lowest surface tension would exhibit the greatest flocculating capacity. This capacity was investigated for a series of sodium salts of organic acids and of hydrochlorides of organic bases, of which the normal solutions show wide variations in the surface tensions. As a general rule no relationship was shown to exist between surface tension of the solutions and flocculation capacity.

In only one case, that of the mastic sol, did such a relationship exist—the hydrochlorides of those bases the solution of which had lower surface tensions precipitating the mastic in lower concentrations. It is suggested by the authors that two classes of suspensoid should exist, namely, those which owe their charge to an ion derived from a salt from which they are obtained by hydrolysis, as, for example, the chlorine ion in the ferric hydroxide sol obtained by dialysis of ferric chloride solutions, and those which owe their charge to an ion derived by dissociation in a colloid acting as an electrolyte in which the active, rapidly moving ion is held electrostatically in an outer layer to the other more slowly moving colloidal ion. The former class are designated exionic and the latter endionic colloids. Mastic belongs probably to the latter class. S. B. S.

Equilibria in the Reduction of Oxides by Carbon. ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON (T., 1919, **115**, 205—214).

Relations between Distribution Ratio, Temperature, and Concentration in System: Water, Ethyl Ether, Succinic Acid. GEORGE SHANNON FORBES and ALBERT SPRAGUE COOLIDGE (*J. Amer. Chem. Soc.*, 1919, **41**, 150—167).—The published data on the solubilities and distribution ratios for this system being insufficiently numerous and concordant, a complete set of new determinations has been made. The ethyl ether used was carefully purified, especially from alcohol, a trace of which may be detected by means of the green coloration given with strong sodium hydroxide solution containing a little permanganate; the presence of 1% of ethyl alcohol is found to increase the solubility of ether in water by about 2%, and that of succinic acid in ether by about 20%, the effect on the solubility of the acid in water being much less. The method of analysis used consisted in shaking a mixture of the desired composition in a "pyrex" vessel shaped like a submarine with periscope; as the stopper is in contact with neither the contents of the vessel nor the water of the thermostat, it need not be greased, danger of contamination being thus obviated. The vessel was rocked at such a speed that the air bubble travelled the whole length to and fro, the rocking being stopped for ten minutes and the two layers extracted separately by inclining the vessel first one way and then the other. Special pipettes were used, which did not require greased stoppers and which allowed of the evaporation of the solutions without transference to other vessels.

The compositions of solutions unsaturated with one of the constituents were determined at 15°, 20°, and 25°, and a series of measurements of the distribution ratio was made at each of the three temperatures and at various concentrations of acid.

If s is the mol. fraction of succinic acid (undissociated) in the water layer, and e, w, σ, ω, and ϵ those of ether in the water layer, water in the water layer, succinic acid in the ether layer, water in the ether layer, and ether in the ether layer, respectively, the com-

plete differential of the distribution ratio ($R=s/\sigma$) with respect to temperature is shown to have the form $dR/dt=(b+an)/\sigma(1-am)-s(\beta+\alpha\nu)/\sigma^2(1-\alpha\mu)$, where $\alpha=[\delta\sigma/\delta\omega]_t$, $\beta=[\delta\sigma/dt]_\omega$, $\mu=[\delta\omega/\delta\sigma]_t$, and $\nu=[\delta\omega/\delta t]_\sigma$. The reasoning involved is followed out by means of a solid diagram. Further, an expression is derived for the value of dR/dt between solutions having constant composition of solvent (compare Herz and Kurzer, A., 1910, ii, 399, 1045), the value thus obtained for dR/dt being 0·0257, whereas the expression given above yields the result, $dR/dt=0·0258$.

Succinic acid is not distributed in constant ratio between water and ether; the ratio of activity to concentration in aqueous solution falls with increasing concentration, or, more strictly, this deviation is greater in water than in ether solution, solvation being undoubtedly largely responsible for this phenomenon.

Application of Rothmund and Wilsmore's mutual solubility equation (A., 1902, ii, 447; compare Nernst, A., 1901, ii, 647) to the solubility data at 20° shows that 60 mols. of H_2O furnish 33 molecules of water, which therefore consist almost entirely of $(H_2O)_2$; this result is only an approximate one, but it agrees well with estimates made by other workers using different methods (compare Richards and Palitzsch, this vol., ii, 97). T. H. P.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIV. Binary Solution Equilibria between Pyrogallol and the Aromatic Amines or Acid Amides. ROBERT KREMANN and LUDWIG ZECHNER (*Monatsh.*, 1918, **39**, 777—805. Compare A., 1918, ii, 69; this vol., ii, 54). —Previous results have led the authors to the conclusion that pyrogallol, as a trihydroxyphenol, should be capable of uniting with three molecules of a primary amine unless the close proximity of the hydroxy-groups leads to steric hindrance. The latter is found to be the case, since pyrogallol unites with only two molecules of aniline, *p*-toluidine or β-naphthylamine, and with but one molecule of α-naphthylamine; with the isomeric phenylenediamines, compounds of the type, 2 molecules pyrogallol + 2 molecules diamine, are obtained, whilst with the para-isomeride there is also formed a compound of two molecules of the phenol with one of the diamine. As is to be expected, an equimolecular compound of pyrogallol and benzamide is found to exist, and a similar compound is in all probability formed from acetamide. H. W.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XV. The Binary Systems of Benzophenone with Phenols and their Derivatives. ROBERT KREMANN and LUDWIG ZECHNER (*Monatsh.*, 1918, **39**, 807—832).—The affinity of different classes of substances towards phenols generally appears to be weakened by the replacement of the methyl by the phenyl group in the former; the work now described was undertaken with the object of obtaining a direct comparison of acetone and benzophenone in this respect.

Benzophenone forms equimolecular compounds with phenol and α-naphthol, thus resembling acetone; with β-naphthol, the three mononitrophenols, the three dihydroxybenzenes, and pyrogallol, on the other hand, it gives simple eutectics. It therefore appears that the ability of a phenol to form compounds with benzophenone is lessened by the introduction into it of groups which strengthen its electronegative character. H. W.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XVI. The Binary Systems of Benzophenone and certain Amines. ROBERT KREMANN and RUDOLF SCHADINGER (*Monatsh.*, 1918, **39**, 833–838).—The inability of benzophenone to yield compounds with negatively substituted phenols (preceding abstract) might be due merely to steric hindrance or to insufficient difference in the heteropolarity of the components, such that whilst the electronegative carbonyl group can react with amphoteric phenol, it is unable to do so with its electronegative derivatives. In the latter case, it appeared probable that benzophenone would react with amines. Experiment, however, shows that it yields simple eutectics with *p*-toluidine and with α- or β-naphthylamine. The difference in behaviour of benzophenone towards phenol on the one hand and towards negatively substituted phenols on the other must be ascribed to steric hindrance. H. W.

Velocity of Reaction in the System $2NO + O_2$. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1919, **25**, 4—9).—Polemical between the author and Bodenstein on the method adopted in calculating from the experimental results in connexion with the above-named system (see Bodenstein, A., 1918, ii, 302; Trautz and Dalal, A., 1918, ii, 162). J. F. S.

Relationship of the Constants of Formation and Hydrolysis of Esters of Symmetrical Dicarboxylic Acids. ANTON SKRABAL (*Monatsh.*, 1918, **39**, 741—763).—A theoretical consideration of the subject and partial review of the literature. The author is led to the following conclusions.

The esterification of a symmetrical dicarboxylic acid and the hydrolysis of its normal ester in the presence of acid lead to an "acid-ester" equilibrium (2 acid ester $\rightleftharpoons$ normal ester + dicarboxylic acid), the constant, K, of which is related to the constant ratios of consecutive hydrolysis and esterification in accordance with the equation $nn' = K$. If, therefore, the acid-ester equilibrium is not appreciably altered by change in temperature and other experimental conditions, nn' must be constant. This is most readily the case when both n and n' are of the order unity, and when, further, $n = n'$. Actually, K is found to be practically independent of the temperature, and its numerical value is frequently 4, hence the simplified constant ratio, $n = n' = 2$. The acid-ester equilibrium is displaced with decreasing acidity, and in consequence the relation-

ship of the constants for alkaline hydrolysis differs from that for acidic hydrolysis.

The esterification of a symmetrical dihydric alcohol and the hydrolysis of its normal ester leads to an "ester-alcohol" equilibrium (2 ester alcohol $\rightleftarrows$ normal ester + alcohol), the constant, K, of which is related to the constant ratios of the consecutive actions according to the equation $nn'=K$. The "ester-alcohol" equilibrium is not influenced by the acidity, and the relationship of the constants is consequently the same for acid and alkaline hydrolysis.

Replacement of the alkyl group is analogous to esterification and hydrolysis. Consecutive replacement in a symmetrical mixed ester leads to the establishment of a "mixed-ester" equilibrium, the constants of which are similarly related to the ratios of the constants for consecutive replacement. The ratios of the constants of the hydrolysis and formation of mixed esters are governed by their relationships to the constants of the two acid-ester equilibria (or ester-alcohol equilibria) and of the mixed ester equilibrium.

The dynamic conception of the ester equilibrium imposes necessary, but not complete, conditions with respect to the relationship of the constants of formation and hydrolysis of symmetrical di-esters and its variation with the experimental conditions. The possible variations are limited by the simultaneous application of the parameter rule (A., 1916, ii, 607). The latter leads to assumptions which can be experimentally tested, and are therefore valuable working hypotheses. H. W.

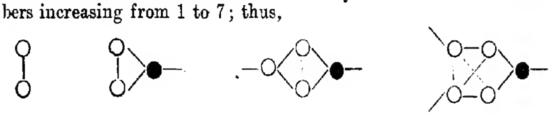
Consecutive Reactions. V. Dynamics of the Oxalic Ester Equilibrium. ANTON SKRABAL and DANICA MRAZEK (*Monatsh.*, 1918, **39**, 697—739. Compare A., 1916, ii, 477; 1917, ii, 250; 1918, ii, 12).—The hydrolysis of normal methyl oxalate, the esterification of oxalic acid, and the reaction of the acid ester in aqueous-alcoholic solution have been kinetically investigated at 25°. The acid titre and the amount of normal ester have been analytically determined at given intervals of time. All three processes show uniformly that the relationship of the constants is 2 : 1 both for the consecutive hydrolysis of the normal ester and for the consecutive esterification of oxalic acid. The esterification equilibrium of oxalic acid has been determined for both stages of the process. H. W.

Hydrolysis of Ethyl Oxalate with Alkali. ANTON SKRABAL and ANTON MATIEVIC (*Monatsh.*, 1918, **39**, 765—773).—To gain insight into the influence of the nature of the alkyl group on the velocity of hydrolysis of esters, the authors have examined the behaviour of ethyl oxalate under conditions similar to those used with the methyl ester (A., 1917, ii, 250). Comparison of the constants obtained with those found for the methyl ester shows the latter to undergo the first stage of hydrolysis three times as rapidly, and the second stage two and a-half times as rapidly, as the ethyl ester. H. W.

Studies in Catalysis. X. The Applicability of the Radiation Hypothesis to Heterogeneous Reactions. WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1919, **115**, 182—193).

Chemical Structure of Atoms. I. FRANZ WENZEL (*J. pr. Chem.*, 1918, [ii], **98**, 155—203).—A theoretical paper containing the following sections:

I. *Typical Elements.*—The author's method of building structural forms of atoms is based on two hypotheses. The first is that the tervalent nitrogen atom is composed of two nuclei united by a double linking (compare A., 1918, ii, 17); in addition to the three valencies, four others are involved in the double linking, thus —●=●<. The second hypothesis is that the mass 14·01 of the nitrogen atom is distributed uniformly over these seven valencies, so that with each valency corresponds a mass of approximately two units, designated valency mass 2. It is assumed, therefore, that to each valency is related a definite mass magnitude. This is usually 2, but in connexion with the atoms of lithium, glucinum, and boron a valency mass 3 must be assumed. Starting, therefore, from the helium atom (composed of two singly linked nuclei) the elements of the first small period can be built up by the systematic addition to both nuclei of the helium atom of valency masses 2 and 3 in numbers increasing from 1 to 7; thus,



He. Li. Gl. B.

(O = valency mass 2; ● = valency mass 3.)

carbon, nitrogen, oxygen, and fluorine are represented by similar structures containing 6, 7, 8, and 9 valency masses respectively. Analogous structures can be formed for the elements of the second period, starting from the neon atom. The author claims that these structures, which are not at variance with the physical properties of atoms, are fitted to express the most important chemical properties of the elements and render possible the treatment of general questions, such as variability of valency and the cause of the metallic and metalloid characteristics of elements.

II. *Valency Masses and their Mode of Linking.*—Assuming that the forces which hold together the valency masses in the atomic nucleus can be treated as valency forces, the maximal value of the valency masses 2 and 3 (and also of valency mass 1, from which valency masses 2 and 3 must be assumed to be derived) can be ascertained. By introducing these maximal values of the valency masses into the structural pictures above, structural formulæ are obtained which allow the deduction of many interesting phenomena, such as (*a*) the existence of a metallic form of the quinquevalent nitrogen atom, on which are founded the ammonium compounds, (*b*) the variations of the atomic weights from whole numbers, (*c*) a

structural formula of the hydrogen atom which appears to account for its metallic properties and for the variation of its atomic weight from exactly 1.

III. *Stereoisomerism of Ammonium Compounds.*—The preceding theory of atomic structure leads to the evolution of a model of the nitrogen atom which is in agreement with crystallographic requirements concerning the spatial positions of the atoms in ammonium iodide and in tetramethylammonium iodide. By the help of this model the possibilities of isomerism to be anticipated in ammonium compounds can be derived. These are exceedingly complicated, and of all the nitrogen models hitherto proposed only the pyramidal formula of Bischoff is applicable for the graphic representation of the isomerism of ammonium compounds, and then only if it is amplified by the insertion of a diagonal in the square base. For the explanation of such isomerism chemistry must call in the help of crystallography in a much greater degree than has hitherto been the case. The isomerism of the optically active ammonium compounds requires for its establishment the conception of a binuclear nitrogen atom.

IV. *The Metallic Carbon Atom.*—It is known that one of the valencies of the carbon atom occasionally functions with basic properties (Baeyer's carbonium valency). This necessitates a "metallic" carbon atom, the structure of which includes the grouping characteristic of the atoms of the metals. Such a structure can be derived from that of the metalloid carbon atom. In the latter the valencies are directed tetrahedrally, whilst in the metallic carbon atom the three metalloid valencies lie in a plane to which the metallic valency lies at right angles, a spacial disposition of the valencies of the metallic carbon atom which the author claims is confirmed by the position of the atoms in the crystal lattice of graphite. C. S.

New Reflux Condenser. James J. Bajda (*J. Ind. Eng. Chem.*, 1919, **11**, 52).—A side-tube, leading from the stem of the condenser just above the flask containing the volatile liquid, conducts the vapours into the top of the condenser jacket, where they enter the condensing coil. The lower part of the latter is formed into a siphon-trap, which delivers the condensed liquid into the flask through a tube extending down the stem of the condenser. A branch tube on the coil just above the trap extends through the top of the condenser jacket. W. P. S.

An Efficient Laboratory Funnel for Filtering Neutral Liquids, especially the Volatile Organic Solvents. T. B. Aldrich (*J. Ind. Eng. Chem.*, 1919, **11**, 139—140).—In this funnel the filter paper is clamped securely between two plates, so that it cannot lift even when the suction is interrupted; the formation of channels and passages for the liquid and precipitate beneath is thus avoided. The funnel is of aluminium and consists of four parts: (1) a cast hollow cylinder with a small flange at the top and a

heavier one at the bottom, both outside, the lower one being screwed; (2) a plate 1·5 mm. thick perforated with 0·75 mm. holes (3 mm. centre to centre); (3) a ring, threaded on the inside and milled on the outside; (4) a conical lower portion provided with a stem and having a flange at the top threaded on the outside to mesh with the threads on the inside of the ring. After the filter-paper has been introduced the ring is screwed up and holds the other three parts together, rubber rings being inserted to render the joints tight. T. H. P.

Inorganic Chemistry.

Chemical Reactions at Low Pressures. IV. The Clean-up [complete removal] of Nitrogen by a Heated Molybdenum Filament. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1919, **41**, 167—194. Compare A., 1915, ii, 467).—When molybdenum filaments are heated at 2000—2400° K in nitrogen at pressures of 40 bars or less (0·03 mm.), great care being taken to exclude moisture, the filaments lose weight at the same rate as if heated in a vacuum. The nitrogen does not attack the filaments, but disappears at a rate independent of the pressure if the latter exceeds 1 bar; the amount of the nitrogen thus disappearing is much less than the chemical equivalent of the molybdenum evaporated, and the ratio, ϵ, of the number of molecules of nitrogen removed to the number of atoms of molybdenum evaporated in the same time decreases from a maximum of about 0·4 to a minimum of about 0·01 as the temperature of the filament or bulb is raised.

With very minute pressures of water-vapour such as result even in presence of drying agents from failure to "bake out" the bulb, no complete removal of nitrogen occurs, although under such conditions molybdenum will remove carbon monoxide and tungsten will remove either nitrogen or carbon monoxide, the value of ϵ in each of these cases being unity.

The fact that ϵ is independent of the pressure, but dependent on the filament and bulb temperatures, indicates that the reaction occurs in the space around the filament, and that each collision between molybdenum atoms and nitrogen molecules results in combination, at least two products being formed; these are probably a first order compound of the formula NMoN and a second order compound, $Mo{:}N_2$, the proportion between the amounts of these two depending on the relative velocity of the molecules at the moment of collision and on the internal velocity of the nitrogen molecules. The former compound is very stable and cannot be decomposed on the bulb by heating to 360°, its formation being favoured by low relative translational velocity of the colliding molecules and by high

internal or rotational velocity in the nitrogen molecule. All those collisions which do not yield the first order compound give that of the second order, which is so unstable that it decomposes practically completely on striking the bulb, owing to the attractive forces between pairs of molybdenum atoms being much greater than between these and nitrogen molecules.

The deposit which collects on the bulb has the following properties. It is spongy and can easily be rubbed off with the finger on opening the bulb, whereas deposits formed in a high vacuum are dense and can scarcely be scratched off with a knife. If the bulb is kept at the temperature of liquid air, the deposit formed gives up some nitrogen when warmed to the ordinary temperature, but only part of this nitrogen is absorbed again on cooling the bulb; the larger part of the nitrogen in the deposit is not, however, liberated by heating in a vacuum at 360°. The deposit very rapidly absorbs up to about one-thirtieth of its chemical equivalent of nitrogen when cooled by liquid air, but it does not readily absorb hydrogen under these conditions. At the ordinary temperature or above, however, large quantities of hydrogen are absorbed or dissolved by the deposit, these being given up slowly at 300° in a good vacuum. When heated in nitrogen at 270° or above, the deposit combines with nitrogen, and this is not given off again at 360° in a vacuum. The deposit reacts rapidly with water-vapour at the ordinary temperature with production of hydrogen, much of which remains dissolved in the deposit until liberated by heating. T. H. P.

Formation of Ammonia by the Electric Discharge. E. BRINER and A. BAERFUSS (*Helv. Chim. Acta*, 1919, **2**, 95—100).—As the result of experiments on the production of ammonia from nitrogen and hydrogen by means of the electric arc it is found that the yield of ammonia is more than doubled when the ratio of nitrogen to hydrogen is increased from 1:3 to 15:3 by volume. This result, which appears to contradict the rule that the optimum mixture for the formation of a substance corresponds with the composition of that substance, is explained on the ground that at the temperature employed the active participants in the reaction are the atoms, not the molecules, of the two gases and that an excess of nitrogen will be necessary if this gas is more difficultly activated than hydrogen. [See also *J. Soc. Chem. Ind.*, 1919, April.]

C. S.

Combustion of Ammonia in a Deficiency of Oxygen. F. RASCHIG (*Zeitsch. physikal. Chem. Unterr.*, 1918, **31**, 138—142; from *Chem. Zentr.*, 1918, ii, 1016—1017).—It is generally considered that the combustion of ammonia in an excess of oxygen results in the formation of nitric oxide and water; the author considers this view to be erroneous, or, at any rate, not proved. When oxygen is in deficit, reaction is commonly supposed to proceed according to the equation (i) $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. Müller (*Zeitsch. physikal. Chem. Unterr.*, 1913, 169) has, however, shown

that under these conditions a quantity of gas is formed containing about 59% nitrogen and 41% hydrogen, and has assumed that a portion of the ammonia dissociates into its constituent elements at the high temperature of the flame. If this were actually the case, considerable quantities of nitrogen should be formed when oxygen is in excess, whereas the yield of nitric acid is actually 90% and over. An explanation may be found in the formation of the hypothetical di-imide when oxygen is in deficit: [(ii) $NH_3+O_2=N_2H_2+2H_2O$], which would probably decompose into nitrogen and hydrogen. The author has heated potassium hydrazinesulphonate with potassium hydroxide in the expectation that the hydroxyhydrazine primarily formed would immediately pass into di-imide by loss of water; actually, the calculated amount of potassium sulphite was formed and a mixture of equal volumes of nitrogen and hydrogen was evolved. A similar result was obtained by the decomposition of benzenesulphonhydrazide, $NH_2{\cdot}NH{\cdot}SO_2Ph$. Müller's experiments can be interpreted by supposing that the combustion of ammonia takes place partly according to equation (i) and partly with formation of di-imide. It is, however, possible that the first reaction does not occur at all, but that combustion proceeds with intermediate formation of hydrazine [(iii) $4NH_3+O_2=2N_2H_4+2H_2O$], which subsequently decomposes into nitrogen and hydrogen. Actually, the author has been able to establish the production of hydrazine (by isolation of benzylazine) when oxygen burns in ammonia. Combustion, therefore, probably proceeds mainly in accordance with equation (ii), and to a less extent according to equation (iii), whilst oxidation in accordance with equation (i) may be considered not to occur at all. H. W.

Formation of Azoimide by Oxidation of Hydrazine. A. ANGELI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 389—393).—The author's experiments (A., 1894, ii, 93) were carried out in accordance with theoretical considerations which referred to the analogies in behaviour shown by hydrazine, hydroxylamine, and hydrogen peroxide, and were completely confirmed experimentally. Browne and Overman (A., 1916, ii, 245) and Sommer (A., 1917, ii, 30), on the other hand, attempted merely to obtain an explanation of a reaction discovered accidentally by them, namely, the formation of azoimide by oxidation of hydrazine, the only connection with the author's work lying in the fact that, to explain the formation of azoimide from hydrazine some intermediate poly-nitrogenated compound must be assumed. This intermediate term is probably tetrazone, $NH_2{\cdot}N{:}N{\cdot}NH_2$ (A., 1917, i, 452; compare Willstätter and Pfannenstiehl, A., 1905, i, 723). T. H. P.

The Oxidation of Nitric Oxide by Dry Air. ANDRÉ SANFOURCHE (*Compt. rend.*, 1919, **168**, 307—310. Compare this vol., ii, 105).—A study of the oxidation of nitric oxide by dry air at temperatures ranging from $-50°$ to $525°$. The first stage in the oxidation, namely, the conversion of nitric oxide into nitrogen

trioxide, is practically instantaneous and independent of the temperature between the limits given. The next stage, the oxidation of the nitrogen trioxide to nitrogen peroxide, is regulated by the reversible reaction, $2N_2O_3+O_2 \rightleftharpoons 4NO_2$, in which the displacement is from left to right up to 200°, but tends more and more towards right to left as the temperature rises from 200° to 525°. W. G.

The Cycle of Oxidation of Nitric Oxide in the Presence of Water. ANDRÉ SANFOURCHE (*Compt. rend.*, 1919, **168**, 401—404).—In the presence of water, nitric oxide is oxidised to nitrogen trioxide and not to the peroxide, the trioxide then being decomposed by the water, giving nitric acid and a partial regeneration of nitric oxide. In the presence of nitric acid (D 1·5), however, the nitrogen trioxide is oxidised with the formation of the peroxide and water, according to the equation $2HNO_3+N_2O_3=H_2O+2N_2O_4$. This oxidation is first noticeable with nitric acid (D 1·3), which has a concentration of approximately 50%, but is not complete, and progresses further as the concentration of the nitric acid used is increased. W. G.

Apparatus [to Demonstrate] the Decomposition of Nitric Acid at a Red Heat. H. BÖTTGER (*Zeitsch. physikal. Chem. Unterr.*, 1918, **31**, 152; from *Chem. Zentr.*, 1918, ii, 1005).—The apparatus consists of a small quartz distilling flask provided with a dropping funnel and connected with an inclined condenser and small glass cylinder; the stopper of the latter carries a glass tube leading to a pneumatic trough for the collection of oxygen. Condenser and cylinder are cooled by a freezing mixture. The nitric acid is allowed to drop into the strongly heated flask; a green liquid, consisting of condensed nitrogen peroxide, water, and unchanged nitric acid, collects in the cylinder. H. W.

Electrochemical Preparation of Salts of Perphosphoric Acid and of Monoperphosphoric Acid. FR. FICHTER and ANTONIO RIUS Y MIRÒ (*Helv. Chim. Acta*, 1919, **2**, 3—26. Compare Fichter and Müller, A., 1918, ii, 439; Rius y Mirò, this vol., ii, 63).—Most of the work has been already published (*loc. cit.*). The amount of monoperphosphoric acid increases with increasing current density, with decreasing total concentration, and with decreasing alkalinity. If the electrolysis is prolonged to produce high concentrations, the current yield decreases largely. With suitable electrodes, the yield of perphosphate is 64% and of monoperphosphate somewhat more than 7%. These salts are formed in moderate yield even in the absence of fluoride provided the electrolyte is rich in alkali; also both peroxidised salts are obtained by the electrolysis of a mixture of tetrapotassium and dipotassium pyrophosphates. In strongly acid solution, perphosphoric acid decomposes spontaneously in about two days into monoperphosphoric acid and phosphoric acid. Monoperphosphoric acid also decomposes in acid solution, but much more slowly than in alkaline solution. C. S.

Graphitic Carbon. V. Kohlschütter (*Zeitsch. anorg. Chem.*, 1919, **105**, 35—68).—The physical and chemical properties of graphite vary within such wide limits that no distinct line of demarcation can be drawn between graphite on the one hand and amorphous carbon or soot on the other. From the consideration of a mass of data relating to the properties and mode of occurrence of natural graphite, and the methods of formation and properties of artificial graphite and amorphous carbon, the author comes to the conclusion that all varieties of graphite and amorphous carbon are different physical forms of "black carbon," which is to be regarded as an allotropic modification of diamond. The properties of different samples of graphite depend on the conditions under which it is produced, and its variable character is to be attributed to different degrees of dispersity. The reactions favourable to the production of graphite fall into three groups: (1) surface reactions; (2) reactions *in situ*; (3) surface layer reactions. These are all reactions of the localised type which have been grouped together in a previous paper in the class of "topochemical" reactions (this vol., ii, 156). As an example of the first group, the decomposition of acetylene by copper at 400—500° produces graphite as the result of a slow surface reaction, whereas the spontaneous decomposition at a higher temperature in unlimited space produces soot. The formation of graphite by the decomposition of a carbide, as in the Acheson process, is an example of the second group, and another example is the precipitation of graphite from iron–carbon solutions, where in all probability crystals of cementite are first formed, which then decompose, leaving the graphite particles as pseudomorphs of the cementite crystals. As examples of the third group, there are those reversible reactions which lead to graphite formation, such as the decomposition of carbon disulphide. In these cases, temperature is of importance only in so far as it determines the rate at which equilibrium is attained. Contrary to the generally accepted view, temperature and pressure have little influence on graphite formation except in so far as they influence other conditions.

It is probable that all natural graphite has been formed by a localised reaction of one of the above types. It may in some cases have been formed by metamorphosis of organic carbon in contact with igneous rock, more often probably by the decomposition of carbon monoxide in clefts, catalysed by the metallic oxides present.

The view that there is no essential difference between graphite and amorphous carbon is borne out by the work of Debye and Scherrer on the constitution of graphite and amorphous carbon (A., 1917, ii, 437), which showed that both have the same interference effect on *X*-rays. The conclusion of these authors that in graphite the carbon atoms are arranged hexagonally in plane layers which are superimposed on one another is in agreement with the present author's idea that graphite owes its peculiar properties to its lamellar structure. This type of structure not only accounts for its peculiar physical properties, but also for many chemical

properties, such as its resistance to oxidation and to reagents, and for the fact that its formation is favoured when free carbon is produced by a surface reaction. The difference between the densities and heats of combustion of graphite and amorphous carbon is discussed, and is shown not to be detrimental to the theory that they are essentially the same form of carbon. The formation of graphitic acid by oxidation of graphite and not of amorphous carbon is due to the peculiar structure of the former and not to the existence of a distinct graphite molecule. E. H. R.

Graphitic Carbon and Graphitic Acid. V. KOHLSCHÜTTER and P. HAENNI (*Zeitsch. anorg. Chem.*, 1919, **105**, 121—144).—For the further elucidation of the structure of graphite (preceding abstract), the oxidation of graphite to graphitic acid and the properties of the latter have been studied. Since the properties of the graphitic acid depend on those of the graphite used, in order to obtain results which could be reproduced, the experiments were confined to a specially pure electrically prepared graphite free from ash. The oxidations were carried out with a mixture of potassium chlorate, nitric and sulphuric acids in the cold under fixed conditions. The peculiar oxidising properties of this mixture are due to the fact that it penetrates the whole mass of the graphite; other oxidising agents which do not penetrate the graphite have little action or oxidise it completely to carbon dioxide.

Repeated treatment of the graphitic acid with the oxidising mixture changes its colour from green to brown or yellow, whilst its carbon content gradually diminishes. Thus after one treatment, the graphitic acid has the composition C=59·02%, H=1·91%, O=39·07%, and after five oxidations, C=54·4%, H=2·14%, O=43·46%. The apparently crystalline particles of graphitic acid are not crystals, but pseudomorphs of the original graphite particles. After repeated washing with water, the graphitic acid passes into solution. The colloidal solution can be flocculated by dilute acids, and the precipitated gel is perfectly soluble in water. The differently coloured graphitic acids merely differ in their degree of dispersity, the more lightly coloured products, obtained by repeated oxidation, being more highly disperse. It is not true, as was formerly supposed, that the colour of the graphitic acid depends on the sample of graphite from which it is made.

When heated or treated with reducing agents, graphitic acid is reduced to carbon. Heating experiments have shown that the gases evolved are water, carbon monoxide, and carbon dioxide, the ratio CO/CO_2 being greater the more slowly the heat is applied. The temperature at which the decomposition becomes explosive is also lower the slower the heating, and if the heating is very slow the decomposition may go quietly to completion without explosion. The black, voluminous residue consists of carbon (99·7% C). It has all the properties of soot, but can be compressed into a mass very similar to graphite. When the decomposition of the graphitic

acid by heat takes place under pressure, the graphitic character of the residual carbon is more marked. By decomposing the graphitic acid under sulphuric acid at 160—180°, a residue was obtained having properties intermediate between those of soot and graphite. Treatment of graphitic acid with reducing agents, such as ferrous or stannous salts, gave products with strongly marked graphitic properties, giving graphitic acid again when oxidised. These products, however, were contaminated with adsorbed iron or tin compounds, which were difficult to remove.

The results of these experiments are held to confirm the opinion expressed in the former paper (*loc. cit.*) that graphite is formed when the reaction resulting in the formation of free carbon is spatially confined (topochemical reaction), and that the difference between graphite and amorphous carbon is purely physical, depending on the conditions of formation. The formation of graphitic acid is likewise topochemical in character, the graphitic acid retaining the structure of the original graphite. E. H. R.

Course of Reaction in Explosions of Dilute Carbon Disulphide-Air Mixtures. G. R. Stewart and John S. Burd (*J. Ind. Eng. Chem.*, 1919, **11**, 130—133).—In the combustion of dilute mixtures of carbon disulphide and air, containing from 2·5 to 4% of the former, from 40 to 60% of the carbon disulphide is oxidised according to the equation $CS_2+3O_2=CO_2+2SO_2$; from 25 to 35% follows the reaction $2CS_2+5O_2=2CO+4SO_2$; the remainder, 15 to 30%, is unchanged. Sulphur trioxide does not seem to be formed. With a mixture containing 2·5% of carbon disulphide, the resulting gases contain about 15% of oxygen, 1% of carbon dioxide, usually less than 1% of carbon disulphide and carbon monoxide, and about 4% of sulphur dioxide. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Precipitated Amorphous Silica. P. Braesco (*Compt. rend.*, 1919, **168**, 343—345).—From a study of the dilatation of precipitated silica, cast into sticks by admixture with 5% of sodium silicate as a paste and subsequently dried and calcined, the author finds that precipitated silica is amorphous provided that it is only heated to about 600°, but that, if it is calcined at a temperature exceeding 1000° it is crystalline and of the same form as cristobalite. W. G.

Nature of the Gas Evolved when Fused Sodium Hydroxide is Dissolved in Water. W. H. Schramm (*Chem. Zeit.*, 1919, **43**, 69—70).—Evolution of gas is sometimes noticed when fused sodium hydroxide is dissolved in water; the greater part of this gas is air contained in the sodium hydroxide, but a small quantity of oxygen, in addition, is also present. For example, 400 grams of fused sodium hydroxide, when dissolved in water free from dissolved gases, yielded 14·45 c.c. of gas containing 28·7% of oxygen. The quantity of oxygen in excess of that due to the air is derived

from the decomposition of an alkali compound of a higher ferric oxide; this compound is present in the sodium hydroxide, and is probably sodium perferrite, $Na_2O{\cdot}Fe_2O_4$. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Normal and Acid Sulphates of Sodium. PAUL PASCAL and ERO (*Bull. Soc. chim.*, 1919, [iv], **25**, 35—49).—A study of the equilibrium of the ternary mixture, Na_2SO_4–H_2SO_4–H_2O, over a temperature range from $-30°$ to $120°$. The results confirm the existence of the following anhydrous salts and hydrates: Na_2SO_4 and its hepta- and deca-hydrates; $Na_2SO_4,NaHSO_4$; $NaHSO_4$; $NaHSO_4,H_2O$; $NaHSO_4,H_2SO_4$; $NaHSO_4,H_2SO_4,1{\cdot}5H_2O$;

$$2NaHSO_4,Na_2SO_4.$$

There was no indication of the formation of the hydrate of the intermediate salt, $Na_2SO_4,NaHSO_4$, or of the hydrate,

$$Na_2SO_4,2{\cdot}5\text{—}3H_2O.$$

Determinations were also made of the temperatures of commencement of solidification of solutions of sodium sulphate in different concentrations of sulphuric acid. Anhydrous normal sodium sulphate is only obtained at the higher temperatures and from dilute acid. From results obtained with solutions of sodium hydrogen sulphate it is shown that, in order to crystallise this sulphate, a considerable quantity of acid must be added to the solution, an acidity equal to 65% sulphuric acid being necessary in order to obtain the anhydrous hydrogen sulphate, the acid sulphates of the type $NaHSO_4,H_2SO_4$ only being obtained with an acidity exceeding 80%.

In order to recover some of the acid from sodium hydrogen sulphate, one of two processes may be adopted. At the ordinary temperature a 40—45% solution of the acid sulphate may be prepared and then cooled to $-20°$, the liquid being sown with a crystal of the decahydrate, $Na_2SO_4,10H_2O$. The liquid separates into a solid phase, and a liquid phase containing at the most 30% of sulphuric acid and about 10% Na_2SO_4. The second method suggested is to prepare a 75% solution of the anhydrous hydrogen sulphate at 100° and cool to the ordinary temperature. The liquid phase obtained contains about 50% of sulphuric acid. [See *J. Soc. Chem. Ind.*, 1919, April.] W. G.

Basic Exchange in Silicates. II. E. RAMANN and A. SPENGEL (*Zeitsch. anorg. Chem.*, 1919, **105**, 81—96).—Experiments have been made on the action of mixed salt solutions on ammonium permutite, prepared by treating sodium permutite with ammonium nitrate. With mixed solutions of potassium and calcium chlorides in equivalent concentrations, the ammonium is completely replaced. The composition of the resulting permutite is independent of the total salt concentration between 0·1 and 3·25*N*. The ratio of the bases in the end-product is generally different from their ratio in the solution, the final permutite containing relatively more of that base of which there is a smaller proportion in the solution. When potassium, ammonium, and, in most cases, sodium are the predomin-

ating bases in the solution, the base ratio in the final permutite corresponds with the ion ratio in the solution. When, however, calcium predominates in the solution, the proportion of calcium in the permutite is much smaller than would correspond with its ion proportion in the solution. Calcium chloride solutions do not bring about complete basic exchange with either ammonium, potassium, or sodium permutite. It is concluded that basic exchange in the case of such silicates as permutite is an ion reaction following the general mass action law, but in the case of calcium, and to some extent sodium salts, a disturbing factor, probably of a physical character, comes into play (compare A., 1917, ii, 468).

E. H. R.

Silver Amalgams Rich in Silver. N. PARRAVANO and P. JOVANOVICH (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 411—412; *Gazzetta*, 1919, **49**, i, 6—9).—Silver amalgams rich in silver were prepared similarly to the gold amalgams (see this vol., ii, 161). The specific electrical conductivity curve is not continuous, but consists of two distinct branches: the first extends from 0 to about 2% of mercury, and has the form characteristic of solid solutions. The second, from about 2% to 14% of mercury (the highest proportion of mercury attainable by the method of preparation used), is a straight line, this being characteristic of alloys composed of two distinct crystalline individuals; the latter are the saturated mixed crystals with 2% of mercury and, according to Reinders (A., 1906, ii, 219), the compound, Ag_3Hg. T. H. P.

[Pure] Calcium Hypochlorite to Replace Dakin's Solution. P. MICHAELIS (*Münch. med. Woch.*, 1919, **66**, 45).—The Griesheim-Electron works manufacture as "hyporit" an almost pure calcium hypochlorite containing a little calcium chloride and very little lime; it has over 80% of available chlorine, and forms a stable powder which can be compressed into tablets of accurate dosage. It readily dissolves in water to an almost clear, very faintly alkaline solution, which replaces that of Dakin. G. B.

Yellow Cuprous Oxide. L. MOSER (*Zeitsch. anorg. Chem.*, 1919, **105**, 112—120).—The best method for preparing yellow cuprous oxide is by the reduction of a cupric salt by means of hydroxylamine in presence of alkali. It can also be prepared electrolytically, using an alkali sulphate as the electrolyte and an anode of pure copper. When a copper salt is reduced by Fehling's solution the character of the precipitated cuprous oxide depends on the relative proportion of tartrate solution used; when excess of tartrate is used, red, crystalline cuprous oxide is formed, but with little tartrate, the cuprous oxide is yellow and amorphous.

As first precipitated the amorphous cuprous oxide is light yellow in colour and is probably a hydroxide. In absence of air the colour quickly changes to orange or brick-red, probably through loss of water. It can then be dried without further change. The dried

product contains a variable quantity, 2—3%, of water, held probably by adsorption. At high temperatures, above a low red heat, the water is lost and the yellow, amorphous oxide changes into the red, crystalline form. The yellow cuprous oxide is to be regarded as a primary metastable form, the red, crystalline form being the stable one. E. H. R.

The Carburation of Ceric Oxide. A. DAMIENS (*Ann. Chim.*, 1918, [ix], **10**, 330—352. Compare A., 1918, ii, 442).—The author shows that the product described by Sterba (compare A., 1902, ii, 399) as an oxycarbide of cerium, $CeC_2,2CeO_2$, is not a definite compound at all. The formation of cerium carbide, CeC_2, in an electric furnace takes place in three stages: $2CeO_2 + C = Ce_2O_3 + CO$, $Ce_2O_3 + 9C = 2CeC_3 + 3CO$, $CeC_3 = CeC_2 + C$. The carbide, CeC_3, is soluble in the cerous oxide, and the intermediate products obtained in the carburation are really solid solutions of this nature, their content of the carbide, CeC_3, varying with the intensity of carburation. This higher carbide in its turn decomposes, giving the known carbide, CeC_2, and graphite, thus accounting for the fact that a pure carbide has never been obtained. W. G.

Disperse Aluminium Hydroxide. I. V. KOHLSCHÜTTER (*Zeitsch. anorg. Chem.*, 1919, **105**, 1—25).—The physical form of any solid substance appearing as the result of a chemical reaction is influenced by the many variable factors which collectively determine the conditions operative at the time of its formation. In particular is this the case when the sphere within which the reaction can take place is limited or localised, as where a solid is formed by a reaction between a second solid and a liquid or gas, the reaction being localised at the surface of the solid. The author's work on the different forms of silver and arsenic (A., 1913, ii, 589, 953) demonstrated the dependence of the physical form of the product on that of the starting material. It is suggested that such strictly localised processes as those here cited should be termed "topochemical" reactions. The study of such reactions is important in connexion with the chemical and physiological processes in plants and animals, and for the study of mineral morphology.

As a noteworthy example of a topochemical reaction, the author has studied the formation of pseudomorphs of aluminium hydroxide by the action of ammonia solution on crystals of aluminium sulphate or ammonium alum. When crystals of either of these salts are immersed in ammonia solutions (1—10*N*), more or less perfect pseudomorphs of the original crystals in aluminium hydroxide are formed, the change being quite rapid and complete. The pseudomorphs can be dried, and sometimes even ignited, without losing their form. The physical characteristics of the pseudomorphs vary very considerably with the reaction conditions, depending especially on the ammonia concentration, temperature, nature of the original crystals, and the nature of the salts present in the reacting solution. For the experiments, crystal particles of graduated sizes were used,

and in order to characterise the resulting pseudomorphs, the average size of the particles was measured after drying at 40°, 110°, and at dehydrating temperature. The pseudomorphs were always smaller than the original crystals, the shrinkage being greater when stronger ammonia solutions were used. The density of the pseudomorphs was always greater from alum than from aluminium sulphate, other conditions being the same. The presence of other salts in the reacting liquor, such as ammonium sulphate, chloride, nitrate, and carbonate, had a considerable influence on the character of the product. The denser pseudomorphs were generally more transparent than the lighter ones.

The pseudomorphs are undoubtedly true gels. After drying at 40° they are rapidly peptised by dilute hydrochloric acid, but after drying at 110° peptisation is slower. The character of the sol obtained varies with that of the pseudomorphs in the same way as their density. The peptisation experiments indicate that the degree of dispersity is greatest in the densest pseudomorphs. The mechanism of the formation of the pseudomorphs and of their peptisation is discussed, the latter being considered a chemical reaction between the hydroxide and acid, as suggested in a previous paper (A., 1916, ii, 485). E. H. R.

The Behaviour of some Alkali Alumino-silicates at High Temperatures. H. Leitmeier (*Zeitsch. anorg. Chem.*, 1919, **105**, 69—80).—The work here described was undertaken to ascertain whether alkali–aluminosilicates, by heating for some time at a temperature just below their melting point, undergo decomposition with loss of alkali to such an extent that the accuracy of the melting-point determination would be affected. Two minerals were examined, a very pure form of orthoclase, adularia, m. p. 1145 ± 5°, and the sodium aluminosilicate, labradorite, m. p. 1245—1250°. Samples of each mineral were kept upwards of 500 hours at a temperature 10° below the melting point. A small and gradually increasing loss of weight was always observed, of the order of about 0·2%. The loss of weight is attributed to loss of alkali, but is too small to confirm by direct alkali estimation. E. H. R.

Purification by Sublimation, and Analysis, of Gallium Chloride. Theodore W. Richards, W. M. Craig, and J. Sameshima (*J. Amer. Chem. Soc.*, 1919, **41**, 131—132).—The method here described for the purification of gallium salts is based on the fact that gallium trichloride sublimes and distils at a low temperature, whereas other chlorides likely to be associated therewith are much less volatile. In the apparatus used, gallium could be burnt in pure, dry chlorine, and the impure gallium trichloride thus obtained distilled in pure chlorine, in nitrogen, and in a vacuum successively; the parts of the apparatus were fused together, so that rubber connexions and ground joints were avoided. Distillation in nitrogen or in a vacuum was found necessary to eliminate dissolved chlorine. The resulting product showed no trace of any other substance in its

spark spectrum when examined in a Hilger wave-length spectrometer. In the best of three preliminary experiments, 0·43947 gram of gallium chloride yielded 1·07087 gram of silver chloride, having required 0·80587 gram of silver for complete precipitation; the values of the atomic weight of gallium calculated from these two data are 70·09 and 70·11 respectively; the determination is to be repeated with larger quantities of the gallium chloride.

T. H. P.

Purification of Gallium by Electrolysis, and the Compressibility and Density of Gallium. THEODORE W. RICHARDS and SYLVESTER BOYER (*J. Amer. Chem. Soc.*, 1919, **41**, 133—134). —The separation of gallium from indium by a method based on the different solubilities of the hydroxides of the two metals in alkali hydroxide solution is incomplete, the gallium thus obtained always containing several per cent. of indium and never showing a higher melting point than 26·9°. Electrolysis in slightly acid solution of a salt of the gallium partly purified by the above process (compare Dennis and Bridgman, A., 1918, ii, 456) yields far better results, the melting point of the gallium deposited being 30·8°, which is higher than any value yet given in the literature.

The compressibility of solid gallium is found to be $2·09 \times 10^{-6}$, this value falling exactly on the curve representing compressibility as a periodic function of the atomic weight; gallium containing several per cent. of indium, as obtained by the hydroxide process, gives an appreciably lower value. For liquid gallium, the compressibility is $3·97 \times 10^{-6}$, a value almost exactly identical with that of mercury and nearly twice as great as that of solid gallium, although its specific volume is less. This result is in agreement with the universal law that solids have compressibilities distinctly less than those of the same substances as liquids, quite irrespective of their specific volumes.

The densities of solid and liquid gallium are 5·885 and 6·081 respectively.

T. H. P.

Influence of Different Factors on the Critical Velocity of Tempering of Carbon Steels. A. PORTEVIN (*Compt. rend.*, 1919, **168**, 346—348. Compare A., 1917, ii, 372).—From a study of the time of tempering as a function of the diameter of homothetic cylinders, and of the hardness as a function either of the time of cooling or of the diameter of the cylinders, it is shown that, for a carbon-steel containing C=1·07%, Mn=0·08%, the ratio τ, time of cooling, to the diameter is given graphically by two straight lines, differing according as the diameter is above 14 mm. or below 13 mm., and at the same time the hardness undergoes a change of about 200 Brinell units. These two phenomena are the consequence of the sudden lowering of the temperature of transformation with cooling and of the change in the microstructure. The critical velocity of tempering, or, more exactly, the region of velocities of cooling in which this sudden change of phenomena occurs, appears to be the most characteristic property of steel in so

far as its tempering is concerned. The critical velocity is also influenced, notably by the manganese content of the steel, decreasing with it. The minimum temperature of hard tempering is a function of the velocity of cooling, and is lower as the velocity is higher.

Chevenard's results, using a steel wire 0·32 mm. in diameter (A., 1917, ii, 414), when compared with the author's results on a cylinder 20 mm. in diameter, made of steel of almost the same carbon and manganese content, lend support to the view that pressure plays an important part in the formation of troostite. W. G.

Some Mixed Crystals of Calcium Ferrite and Aluminate. EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1919, **11**, 116—120. Compare *ibid.*, 1913, **5**, 627; 1915, **7**, 835; A., 1914, ii, 772).—Cooling curve and micrographic investigations have been carried out in order to ascertain (1) if a calcium ferrite of the composition $5CaO,3Fe_2O_3$ really exists (compare Shepherd, Rankin, and Wright, A., 1911, ii, 725; Rankin and Wright, A., 1915, ii, 50; Sosman and Merwin, A., 1916, ii, 618), and (2) what is formed when a mixture of calcium oxide, ferric oxide, and alumina is melted and then cooled slowly enough to permit the material to be nearly in equilibrium during the entire cooling period. The results obtained confirm the statement that dicalcium ferrite, $2CaO,Fe_2O_3$, and monocalcium ferrite, CaO,Fe_2O_3, are the only definite compounds of lime and ferric oxide. Pure tricalcium aluminate, $3CaO,Al_2O_3$, may be recovered by crystallisation from a solution of lime in the compound, $5CaO,3Al_2O_3$, as a solvent provided that the concentration of the lime at the beginning of the crystallisation is less than is required to form tricalcium aluminate with all the alumina present. If a solution with the empirical formula $8CaO,3R_2O_3$, containing ferric oxide and alumina in the molecular proportion 1:3, is slowly cooled, mixed crystals with the ferric oxide and alumina in the ratio 1:7 crystallise out until the ratio $Fe_2O_3:Al_2O_3$ in the solution has been increased to 3:5; mixed crystals in the latter ratio then crystallise out, further increase in the $Fe_2O_3:Al_2O_3$ ratio being produced until, at about 1370°, the ratio reaches the value 1:1. Those aluminates in which part of the alumina is replaced by ferric oxide are capable of holding in solution less calcium oxide than the pure aluminates. T. H. P.

A New Method of Determining the Allotropic Transformation of Nickel. ERNST JÄNECKE (*Zeitsch. angew. Chem.*, 1918, **31**, i, 229; *Zeitsch. Elektrochem.*, 1919, **25**, 9—17).—Allotropic changes in metals are accompanied by a change in the rate of expansion, which, however, is so small that it is difficult to detect. The following method allows the change to be observed over short as well as long intervals of time. A nickel cylinder, 45 cm. long, is inserted in a low-pressure press (3000 kilos.) used for textile and compressive strength tests, and heated by means of a resistance furnace. The variation in length produces a movement of the upper movable plate of the press, which can be registered; move-

ments as small as 0·007 mm. are indicated. The transformation temperature of nickel is 347—360°; the expansion graph consists of two straight lines, that above the transformation temperature being the more steeply inclined. W. R. S.

Molecular Compounds with High Co-ordination Numbers and with Atomic Groups as Co-ordination Centres. The Stereochemistry of Inorganic Boron, Silicon, and Phosphorus Compounds. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1919, **105**, 26—34).—The type of crystal structure which has been revealed by the study of crystals by means of X-rays can be explained chemically on the assumption that the crystal is a complex molecular compound of the co-ordinated type. It is necessary, however, to assume that not only atoms, but also groups of atoms, may function as co-ordination centres, and that co-ordination numbers as high as 8 or 12 are possible. The distribution of the co-ordinated groups around the central atom or group can be represented by reference to a cube. When the co-ordination number is 4, the co-ordinated groups occupy alternate corners of the cube (tetrahedral grouping); six similar groups occupy face centres (octahedral grouping); eight groups occupy all cube corners (cubic grouping), and twelve groups are situated at the centres of cube edges (cubo-octahedral grouping). The author proceeds to show that a number of known compounds may be represented as co-ordinated compounds with co-ordination numbers 8 or 12. Among the former are included compounds of the type $[Mg(OH_2)_8]Cl_2$, $[Mg(OH_2)_8]BiCl_5$, $[Al(OH_2)_8]_2(SO_4)_3$, $[Ca(NH_3)_8]Cl_2$, and the well-known series of double nitrates of the rare earths of the type $[M''(OH_2)_8]_3[M'''(NO_3)_6]_2$. A number of double fluorides, cyanides, and oxalates are also included.

The alloys of the type $NaZn_{12}$, KHg_{12} are typical molecular compounds of the 12-co-ordinated type, and should have the same crystalline structure as the metals copper, silver, and gold. The alums can also belong to this type, $[M'''(OH_2)_{12}](SO_4)_2M'$, and also a number of dodecahydrates of metallic salts. Specially interesting in this connexion are the phospho-, silico-, and borotungstates described by Rosenheim and Jänecke (A., 1918, ii, 77). The respective tungstic acids may be represented by the formulæ:

$$\left[\left(P{}^{O''}_{O_5{}'}\right)(WO_3)_{12}\right]H_7. \quad \left[\left(Si{}^{O_2{}''}_{O_4{}'}\right)(WO_3)_{12}\right]H_8. \quad \left[\left(B{}^{O_3{}''}_{O_3{}'}\right)(WO_3)_{12}\right]H_9.$$

In these formulæ, the central atom (P,Si,B) has six co-ordinated oxygen atoms, and the group (RO_6) itself functions as a co-ordination centre with twelve co-ordinated (WO_3) groups. In the group (RO_6) it is necessary to distinguish two kinds of oxygen atoms in order to account for the number of ionised hydrogen atoms in the molecule. This distinction brings in the possibility of the existence of isomerides, since the groups $\left(Si{}^{O_2{}''}_{O_4{}'}\right)$ and $\left(B{}^{O_3{}''}_{O_3{}'}\right)$ when given an octahedral space configuration can have both *cis* and *trans* forms. These considerations are in perfect agreement with

the facts, for both silicotungstates and borotungstates of this type are known in two forms, whereas no isomerism has been observed in the case of the phosphotungstates. E. H. R.

Investigation by means of *X*-rays of the Crystal Structure of White and Grey Tin. A. J. BIJL and N. H. KOLKMEIJER (*Proc. K. Akad. Amsterdam*, 1919, **21**, 494—500, 501—504).—From the photographs of white and grey tin previously obtained (this vol., ii, 108), the crystal structures of the two forms have been deduced. T. H. P.

Gold Amalgams Rich in Gold. N. PARRAVANO and P. JOVANOVICH (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 364—368; *Gazzetta*, 1919, **49**, i, 1—6. Compare this vol., ii, 69, 155).—Previous investigations by various authors lead to the conclusion that in gold amalgams containing between about 90% and 100% of gold, mercury exists dissolved in the gold to form solid solutions. In order more clearly to define the nature of these gold amalgams rich in gold, the authors have measured the electrical resistances at 25° of pure gold and of a series of twenty-one of the amalgams containing from 0·4859% to 9·593% of mercury. These amalgams were prepared by coating gold wire about 0·5 mm. in diameter electrolytically with mercury, heating the wire at 200° for two to three hours, then coating again with mercury and heating, this procedure being continued until the resulting amalgam assumed the desired composition. The homogeneity in composition of the amalgamated wires was demonstrated by microscopic examination and also by analysis. The specific conductivities of the different amalgams are given in the forms of a table and a curve, the latter showing a continuous diminution in the conductivity of gold by increasing proportions of mercury. This behaviour is characteristic for solid solutions. T. H. P.

Action of Alkalis on Crucibles made of Alloys of Platinum or of Gold. PAUL NICOLARDOT and CLAUDE CHATELOT (*Bull. Soc. chim.*, 1919, [iv], **25**, 4—9).—Platinum crucibles undergo marked corrosion when sodium hydroxide or potassium hydroxide is fused in them, and the crucibles are subsequently washed, first with water and then with dilute acid. New crucibles resist better than old crucibles, and the presence of iridium rather diminishes the resistance to corrosion. Potassium hydroxide is decidedly more corrosive than sodium hydroxide. In the case of crucibles of alloys of gold, those made from gold–palladium alloys were the most resistant to the fused alkali hydroxides, but even this alloy was very seriously attacked by sodium peroxide at the concentration necessary for the decomposition of minerals such as chromite. Barium oxide at 825° is much less corrosive than the alkali hydroxides. W. G.

Mineralogical Chemistry.

Volcanic Explosions. I. Explosive Eruptions and their Phases. Combustion of Hydrogen. VENTURINO SABATINI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 360—364).—Water-vapour alone is capable of explaining the mechanical effects produced in volcanoes and the projections from the latter, and there is evidence indicating that water-vapour constitutes almost the whole of the gaseous products of volcanic smoke columns; the source of this vapour is not yet established. At the high temperatures prevailing in the depths of volcanoes, the water-vapour is easily decomposable by various elements, with liberation of hydrogen; actual dissociation of the water-vapour to any large extent is improbable owing to the high pressures existing.

The presence of water in the lava may be derived from water of infiltration meeting the very hot lava and being absorbed and decomposed by it, the hydrogen and any residual uncombined oxygen passing up into the crater and there meeting the atmospheric oxygen entering through the fissures, and thus giving rise to violent explosion. The law connecting pressure and temperature inside the laval mass is not known, but it is probable that the latter does not increase at the same rate as the former. At the high temperatures prevailing at great depths, the hydrogen remains gaseous, and at 2000° reaches its maximal density (co-volume).

Laboratory experiments show that the minerals formed at the highest temperatures are spinels, melting at 1900°, whilst iron chromate melts at 1850°, quartz at 1775°, and peridotes at 1730° or above; others generally melt below 1700°. Thus at 2000° or, under high pressures, at a considerably lower temperature lava cannot contain elements in the solid condition. T. H. P.

Volcanic Explosions. II. Calculations on the Combustion of Hydrogen. Comparison with Ordinary Explosives. VENTURINO SABATINI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 405—407. Compare preceding abstract).—The energy developed in the explosion of one-ninth of a kilogram of hydrogen, with a co-volume of 1240 litres, is considered, and it is shown that 800,000 kilogram-metres remain available for rupturing the cup of the crater, for enlarging the latter, and for projecting matter therefrom, a loss of one-third of the energy in heat effect and in secondary shocks being assumed. With glyceryl nitrate and explosive gelatin, the corresponding amounts of energy given per kilogram are 625,000 and 652,000 kilogram-metres respectively. T. H. P.

Mimetite, Thaumasite, and Wavellite. E. T. WHERRY (*Proc. U.S. Nat. Mus.*, 1918, **54**, 373—381).—Colourless, acicular crystals from the Tintic district, Utah, were thought to be penfield-

ite until it was observed that they had different optical constants ($\omega = 2{\cdot}14$, $\epsilon = 2{\cdot}13$). An analysis made on 6 mg. proves them to be mimetite: PbO 73·3, Cl 2·5, As_2O_5 [24·7]%.

Crystals of thaumasite are described from West Paterson, New Jersey. Although minute, these give the axial ratio $a:c = 1:0{\cdot}931 \pm 0{\cdot}003$, and several new forms. Thaumasite is described chemically as "di-hydroxy-tricalcium carbono-silico-sulphate crystallising with $14H_2O$ in the hexagonal system."

Wavellite, as divergent groups of minute, acicular crystals in ferruginous sandstone from Hellertown, Pennsylvania, gives the new axial ratio $a:b:c = 0{\cdot}564:1:0{\cdot}404$. Analysis by F. Wynkoop agrees with the formula $(Al[OH,F])_3(PO_4)_2 + 5H_2O$ of Groth, rather than with that of Dana:

Al_2O_3.	P_2O_5.	SiO_2.	F.	H_2O.	Total.	Sp. gr.
36·5	33·4	1·1	0·8+	28·6	100·1	2·325

L. J. S.

Connexion between the Optical Constants and Chemical Composition of the Scapolites. N. Sundius (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 1—12).—The following determinations support the statement of Borgström (A., 1915, ii, 836) that in the minerals of the scapolite group the refractive indices and the double refraction increase with the percentage of carbon dioxide present. I, small, yellow grains with pyroxene from Hesselkulla, Sweden. II, fine-grained, crystalline material with calcite, pyroxene, etc., from Waldviertel, Lower Austria. III, white, fine-grained with little muscovite and calcite, from Froland, Arendal, Norway. IV—VI, from Vahâive, Pahtosvaara, and Kalpivaara respectively, all in the Kiruna district, Swedish Lapland:

	Chloride-marialite.	Sulphate-marialite.	Carbonate-marialite.	Sulphate-meionite.	Carbonate-meionite.	ω	ϵ	$\omega - \epsilon$.
I.	3	—	27	—	70%	1·5880	1·5534	0·0346*
II.	4	—	36	—	60	1·583	1·549	0·035
III.	71	2	—	—	27	1·5516	1·5427	0·012
IV.	36	6	—	—	58	1·575	1·550	0·025
V.	71	—	—	6	23	1·554	1·541	0·0134
VI.	75·5	—	—	3	21·5	1·550	1·540	0·0101

* I, sodium-light; II—VI, daylight.

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	Cl.	SO_3.	CO_2.	H_2O.	Total.	Sp.gr.
I.	45·53	28·41	17·49	n.d.	0·10	0·04	4·61	n.d.	96·18	2·730
II.	48·60	27·07	15·69	n.d.	0·17	0·02	4·48	0·23	96·26	2·710
III.	56·82	22·14	7·51	7·64	2·89	0·22	1·14	1·08	100·12*	—

* Incl. K_2O, 0·72.

L. J. S.

Composition of Tourmaline from Utö, Sweden. HJ. SJÖGREN (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 317—324).—The occurrence of tourmaline of different colours in the lithia-bearing pegmatite veins of the Island of Utö, near Stockholm, has long been known. Analyses by N. Sahlbom are of I, the pink variety ("rubellite"); II, pale green; III, greyish-white, nearly colourless; IV, bluish-black. The first three are alkali-tourmalines, and the last an iron-tourmaline. Details are given of the method of analysis. Some of the iron is perhaps present in the ferric state, especially in IV. The results agree closely with the general formula, $H_{20}B_2Si_4O_{21}$, of Penfield and Foote (A., 1899, ii, 304):

	SiO_2.	B_2O_3.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Li_2O.	P_2O_5.
I.	36·70	10·76	42·99	1·35	0·28	0·60	0·10	0·49	3·36	0·89	nil.
II.	36·48	9·74	40·08	3·51	0·40	trace	0·08	0·86	2·99	1·11	0·17
III.	36·33	9·79	40·99	1·35	0·37	0·95	0·16	0·50	3·04	1·31	nil.
IV.	35·40	10·45	34·69	9·04	0·41	1·08	0·89	0·60	3·15	0·72	0·13

	F.	$H_2O < 105°$.	$H_2O > 105°$.	Total less O for F.
I.	0·19	0·24	2·75	100·62
II.	0·40	0·17	3·85	99·64
III.	0·39	0·45	4·02	99·46
IV.	0·29	0·09	2·64	99·46

L. J. S.

Analyses of Swedish Glauconites. NAIMA SAHLBOM (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 211—212).—Analysis I is of material from coarsely crystalline Silurian limestone at Eriksöre, Öland. The glauconite was separated from the crushed rock by means of an electromagnet and pure grains picked out under a lens. The grains are olive-green and sharply angular with rough surfaces. Brown, weathered grains were rejected. The material is slowly decomposed by hot hydrochloric acid. At 100° it loses 1·60% H_2O. II is of material mixed with quartz grains from Schonen. The grains are irregularly rounded, with dull lustre and dark green colour; they more closely resemble the ordinary type of glauconite than I. The material is difficultly attacked by hot hydrochloric acid. It loses 2·7—3% H_2O at 100°:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.
I.	51·35	9·47	16·37	4·75	0·63	3·17	7·34
II.	52·74	12·29	9·35	6·30	0·55	4·05	7·97

	Na_2O.	F.	P_2O_5.	H_2O. > 100°.	Total.	Sp. gr.
I.	1·22	—	0·35	4·85	99·50	2·82
II.	0·09	0·13	—	5·93	99·40	2·73

L. J. S.

The Eulysite of Södermanland. JOHN PALMGREN (*Bull. Geol. Inst. Univ. Upsala*, 1917, **14**, 109—228).—Eulysite is a dark, fine-grained olivine-augite-garnet rock occurring as beds in gneiss at Tunaberg and several other places in central Sweden. It is

usually classed with the peridotites and sometimes with eclogite; the present author regards it as a crystalline schist. The following minerals were isolated from the rock for optical examination by the Fedorov "universal method." The olivine is a manganfayalite; analysis I is of honey-yellow grains picked out from the crushed rock from Gillinge, and II of the portion soluble in dilute hydrochloric acid of the rock from Tunaberg. Diopside from the Gillinge rock gave III, corresponding with $CaMgSi_2O_6$ 19%, $CaFeSi_2O_6$ 61%, and $MgFeSi_2O_6$ 20%. Iron-anthophyllite (IV) from Tunaberg shows a distinct prismatic amphibole cleavage and straight extinction; birefringence, negative, $\gamma - \alpha = 0·020$, optic axial angle $2V = 89°6'$. The analysis corresponds with $3FeSiO_3 + RSiO_2$, where R = Mg, Mn, Ca. The mineral is very similar to that from Rockport, Massachusetts (Warren, A., 1904, ii, 45). Analysis V is of hornblende from Gillinge. Grünerite, from Strömshult, Tunaberg, with extinction angle $(c:\gamma) = 14·5°$, gave VI, corresponding with $FeSiO_3 + RSiO_3$. The relation of this to other monoclinic iron amphiboles is discussed. VII of potash–felspar, mainly microcline with some orthoclase, from Gillinge. Garnets at Tunaberg are represented by almandine (anal.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	28·22	—	—	—	63·20	5·19	0·50	2·32	—	—	—	99·43	4·32
II.	31·62	—	0·46	—	35·12	26·51	1·58	4·39	—	—	—	100·00	—
III.	49·84	—	0·78	0·50	19·85	3·66	6·90	18·42	—	—	0·35	100·30	3·544
IV.	47·46	0·03	0·14	0·34	42·34	3·88	1·05	5·05	—	—	0·07	100·25	[illegible]
V.	37·30	0·93	12·75	7·18	19·73	1·42	11·46	4·94	2·67	0·90	1·22	99·93*	3·35
VI.	50·79	0·07	0·55	0·84	30·64	5·98	1·42	7·87	—	—	1·87	99·98	3·306
VII.	65·15	—	18·14	0·57	—	trace	0·08	trace	14·08	1·27	0·41	100·19†	2·595
VIII.	37·21	0·02	19·37	2·56	23·48	11·04	5·75	0·58	—	—	0·15	100·16	4·115
IX.	37·11	0·10	19·68	1·93	7·72	26·45	6·39	0·75	—	—	0·11	100·24	4·09
X.	47·92	—	0·16	0·46	13·78	27·96	6·20	3·58	—	—	0·28	100·34	3·60

* Also F, 0·17. † Also BaO, 0·49.

VIII) and spessartite (IX); the former is intermediate in composition between typical almandine and spessartite, and is called manganalmandine. Veins in a richly manganiferous eulysite at Tunaberg are filled with a pyroxenic mineral (named *sobralite*), together with manganfayalite and spessartite. In hand-specimens the former is brown with a lilac tinge. Analysis X is of opaque, pale lilac grains, and corresponds with $4MnSiO_3$, $2FeSiO_3$, $CaSiO_3$, $MgSiO_3$. Optical examination shows it to be triclinic with cleavages in three directions, and to differ from pyroxmangite (Ford and Bradley, A., 1913, ii, 869) in the position of the optic axial plane. Analyses, also by R. Mauzelius, are given of the rock and of the associated iron-ores and limestones.

L. J. S.

Analytical Chemistry.

Ring Formation in Reactions. F. REISS and G. DIESSELHORST (*Chem. Zeit.*, 1919, **43**, 39).—Certain reactions, such as the blue coloration given by nitrates with diphenylamine and sulphuric acid, are characterised by the formation of a ring, preceding the production of a coloured zone. This is due to adhesion between the liquid and the glass of the tube, and the greater the surface of contact the more sensitive is the reaction. C. A. M.

Use of Filter-paper Pulp in Analysis. O. HACKL (*Chem. Zeit.*, 1919, **43**, 70—71).—The addition of a quantity of filter-paper pulp is advantageous in the filtration of such precipitates as barium sulphate, calcium oxalate, sulphur, ferric hydroxide, aluminium hydroxide, etc., but it should not be used in the last two instances when it is desired to re-dissolve the precipitates in hot hydrochloric acid. A precipitate of ferric hydroxide mixed with filter-paper pulp, when ignited, forms a finely divided powder which dissolves readily in hydrochloric acid. In the case of filtration of silica from a solution containing aluminium salts, the presence of filter-paper pulp retards the rate of filtration. [See, further, *J. Soc. Chem. Ind.*, 1919, 235A.] W. P. S.

The Replacement of Platinum by an Alloy in Apparatus for Electrolytic Analysis. PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1919, [iv], **25**, 84—86. Compare A., 1918, ii, 425).—For the preparation of cathodes, the authors recommend the use of an alloy of gold and copper in the proportion of 9:1 in place of platinum. The total loss in weight of such a cathode, weighing 23·5 grams, was only 0·001 gram during twenty estimations of different types. Anodes may be prepared from the same alloy, but should be coated with a thin layer of platinum electrolytically deposited. W. G.

Apparatus. H. VIGREUX (*Ann. Falsif.*, 1918, **11**, 385—387).—*Apparatus for the Estimation of Ammonia.*—The distillation flask is connected with a vertical fractionating column, the upper part of which is connected with a slightly inclined condensing apparatus. The latter condenses the steam, and the greater part of the condensed water returns through the column into the flask, whilst the ammonia vapours pass to an absorption vessel. *Safety Valve for Water Pumps.*—The valve, which is placed between the pump and the vessel from which the air is to be exhausted, consists of a vertical chamber containing a float; if water flows back from the pump and enters the lower part of the chamber, the float rises and cuts off connexion with the other portions of the apparatus. *Condenser.*—Numerous cross tubes are provided in the inner tube

of an ordinary Liebig condenser; these tubes provide a free passage for the water in the jacket and increase the available condensing surface. [See, further, *J. Soc. Chem. Ind.*, 1919, 200A.]

W. P. S.

Absorption Pipettes. E. van Alstine (*J. Ind. Eng. Chem.*, 1919, **11**, 51—52).—Two vertical cylindrical bulbs, placed one above the other, are connected by a short length of glass tubing, the centre portion of which is constricted to a capillary. A side-tube connects the top of the upper bulb with the tube below the capillary. The bottom of the lower bulb is, by a swan-neck tube, connected with the top of a third bulb, and this, in turn, with a fourth bulb. For use, the absorption solution contained in the fourth bulb is drawn over so as to fill the two cylindrical bulbs; the gas (for example, air containing carbon dioxide) is admitted from the measuring burette into the top of the upper bulb and passes into the lower bulb through the side-tube. Meanwhile, the solution passes gradually through the capillary and continually wets the interior wall of the lower bulb, which now contains most of the gas. Some absorption also takes place in the third bulb, the fourth bulb serving as a reservoir for the solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 201A.] W. P. S.

Simplified Gas Analysis: Burette without Stopcocks for Gas Analysis. J. J. R. Macleod (*J. Lab. and Clin. Med.*, 1918, **4**, 69—72; from *Physiol. Abstr.*, 1919, **3**, 553—554).—The apparatus is designed for teaching purposes, and is based on that of Haldane. The chief differences are that it has screw clips instead of stopcocks, and a special "pressure adjuster" to adjust the gas pressure in the burette after the screw clips have been tightened.

W. G.

Method for the Extraction and Estimation of Dissolved Gases in Water. F. W. Richardson (*J. Soc. Chem. Ind.*, 1919, **38**, 32—33T).—A strong glass bottle of about 1 litre capacity is filled with the water. The lower tube of a bulb or funnel provided with two taps is passed through a rubber stopper, the air is exhausted from the bulb, and the stopper is inserted in the bottle, thereby connecting the tube with the water. When the tap is opened a small quantity of the water enters the bulb, evolution of gas at once begins, and, if the bottle is placed in water at about 40° and the gases removed occasionally from the bulb, the water will continue to boil until all the gases have been expelled and collected. W. P. S.

Estimation of Chlorate and Perchlorate in Potassium Nitrate. A. Wogrinz and J. Kuber (*Chem. Zeit.*, 1919, **43**, 21—22).—The methods described by Förster (A., 1899, ii, 57), Tschernobéev (A., 1905, ii, 416), Winteler (A., 1898, ii, 90), and Hendrixson (A., 1904, ii, 679) were found to be trustworthy.

W. P. S.

Rapid Method of Estimating Sulphide Sulphur in Pyrites. A. BARTSCH (*Chem. Zeit.*, 1919, **43**, 33—34).—On heating pyrites with hydrobromic acid in the presence of metallic mercury the whole of the sulphide sulphur is liberated as hydrogen sulphide. Air is expelled from the apparatus, and the last traces of hydrogen sulphide afterwards driven forward by means of a current of carbon dioxide. The hydrogen sulphide is absorbed in an acetic acid solution of cadmium acetate or of zinc acetate and cadmium acetate, and is subsequently estimated by an iodometric method. [See also *J. Soc. Chem. Ind.*, 1919, 171A.] C. A. M.

Estimation of Phosphorus in Vanadium Steels, Ferrovanadium, Non-vanadium Steels, and Pig Iron. CHAS. MORRIS JOHNSON (*J. Ind. Eng. Chem.*, 1919, **11**, 113—116).—The methods here described make use of a faintly ammoniacal ammonium molybdate solution, which is easy to prepare and convenient to handle, and keeps clear indefinitely. The true phosphorus content of ferrovanadium containing as much as 56·7% of vanadium may be estimated. [See, further, *J. Soc. Chem. Ind.*, 1919, 179A.] T. H. P.

Organic Phosphorus of Soil: Experimental Work on Methods for Extraction and Determination. J. C. SCHOLLENBERGER (*Soil Sci.*, 1918, **6**, 365—395. Compare Potter and Benton, A., 1917, i, 76).—Very full details are given for the estimation of inorganic phosphorus and total phosphorus in the soil, using Neumann's wet combustion for the latter. For the preliminary removal of bases, prior to the extraction of organic phosphorus, it is recommended to wash the soil with 1% hydrochloric acid until 50 c.c. of the extract no longer contains any calcium, after which the acid is washed out by means of a saturated solution of carbon dioxide. The residual soil is then extracted with 4—6% ammonium hydroxide, using 400 grams of soil per litre and shaking two to eight hours, the extract being subsequently filtered through a layer of the soil on a Buchner funnel, this process taking one to three days, and being the most satisfactory for the removal of clay from the extract. Sodium or potassium hydroxide is no more efficient than ammonium hydroxide in extracting organic phosphorus from the soil, and one extraction by the latter alkali, using the proper procedure, removes from the soil practically all the organic phosphorus that is capable of being taken into solution.

No constant relation was observed between total organic matter and organic phosphorus in the ammoniacal extracts, although, as a general rule, they varied in the same direction. For a given soil, it was found that the humus and organic phosphorus in, and the colour of, the ammoniacal extracts, and the total nitrogen content of the soil in the four layers, 0—6 in., 6—12 in., 12—18 in., and 18—24 in., are present in the same relative proportions in each layer. W. G.

The Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. J. CLARENS (*Bull. Soc. chim.*, 1919, [iv], **25**, 87—90. Compare A., 1918, ii, 128).—A reply to Villiers (compare A., 1918, ii, 333).
W. G.

Estimation of Boric Oxide in Glass. J. D. CAUWOOD and T. E. WILSON (*J. Soc. Glass Tech.*, 1918, **20**, 246—252).—Sullivan and Taylor's modification (*Chem. News*, 1915, **111**, 64) of Wherry's method (A., 1910, ii, 92) yields trustworthy results in all cases, whilst Wherry's method itself is untrustworthy when the glass contains much zinc or lead. In the modified method, the sodium carbonate fusion is dissolved in water, the insoluble zinc, lead, etc. carbonates are removed by filtration, and the filtrate then acidified and treated as in Wherry's method. W. P. S.

Micro-elementary Analysis of Organic Substances. J. V. DUBSKY (*Helv. Chim. Acta*, 1919, **2**, 63—75).—A description of the methods of estimating carbon, hydrogen, and nitrogen by micro-analysis. The advantages of a new micro-balance, by P. Hermann, are enumerated. C. S.

Microelementary Analysis of Compounds containing Sulphur, Halogens, and Oxidised Nitrogen. Double Combustion. CH. GRÄNACHER (*Helv. chim. Acta*, 1919, **2**, 76—84).—To avoid obtaining high results in the estimation of carbon in organic compounds containing sulphur and halogens, and particularly in highly nitrated substances, the author employs a layer of lead peroxide 5 cm. in length at the forward end of the combustion tube beyond the silver roll. The lead peroxide must be maintained at a temperature between 170° and 180°, and this is secured by surrounding this portion of the combustion tube with a copper chamber containing boiling aniline.

A "universal tube" suitable for the combustion of any substance obtained in the organic laboratory is one filled from the boat forwards with (1) silver roll, (2) mixture of equal parts of copper oxide and lead chromate, (3) silver roll, and (4) lead peroxide.

Arrangements of apparatus are described whereby the estimation of the nitrogen or of the carbon and the hydrogen in two substances in two tubes side by side can be performed simultaneously. C. S.

The Red Iodotannic Reagent. D. E. TSAKALOTOS and D. DALMAS (*Bull. Soc. chim.*, 1919, [iv], **25**, 80—84).—The sensitiveness of the iodotannic reaction (compare A., 1918, ii, 454) is much greater than that of starch-iodide, especially for very dilute solutions of iodine, but the reaction is interfered with by the presence of potassium iodide, which, on the other hand, increases the sensitiveness of the starch-iodide. An excess of either iodine or tannin inhibits the formation of the red colour in the iodotannic reaction. W. G.

Estimation of Cadmium by the Hydrogen Sulphide Method. EDWARD SCHRAMM (*J. Ind. Eng. Chem.*, 1919, **11**, 110—113).—The literature of the estimation of cadmium and the general considerations governing it are discussed, and a method described which permits of the accurate estimation of cadmium in brass. [See *J. Soc. Chem. Ind.*, 1919, 181A.] T. H. P.

A Very Sensitive Reaction of Copper. Application to the Analysis of Ashes and of Arable Soils. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1919, **168**, 489—492).—When potassium ferrocyanide is added to a very dilute solution of copper chloride in hydrochloric acid in the presence of a zinc salt so that the copper and zinc are in the proportion of 1:4 or 5, the liquid is first tinged yellowish-red, but gradually a precipitate forms which when separated is seen to be blue. This is a very delicate test for copper in the absence of iron, manganese, or nitric acid, and may be applied to the detection and estimation of traces of copper in plant ashes if the copper is first separated electrolytically. [See *J. Soc. Chem. Ind.*, 1919, 235A.] W. G.

Estimation of Iron in Ores by Permanganate. ROBERT SCHWARZ and BERNHARD ROLFES (*Chem. Zeit.*, 1919, **43**, 51).—In the estimation of ferrous chloride in hydrochloric acid solution a mixture of manganese sulphate and phosphoric acid is added to inhibit the oxidation of the hydrochloric acid by the permanganate. This, however, is not perfectly effective; the results are always high, and hitherto it has been customary to correct this error by standardising the permanganate under the conditions under which it is used in the titration, thereby employing a false standardisation value. The authors have found that colloidal silicic acid exerts a perfect protective action, when used in addition to the manganese sulphate and phosphoric acid mixture, and that correct results are then obtained with permanganate standardised by any of the usual methods. About 4—5 grams of the ore are dissolved in 40—60 c.c. of boiling, strong hydrochloric acid, and the solution made up to 500 c.c. Fifty c.c. of the liquid are reduced with stannous chloride, the excess of the latter removed by mercuric chloride, 10 c.c. of the manganese sulphate and phosphoric reagent are added, and about 5 c.c. of a solution of "water-glass," D 1·17, 1 c.c. of which contains about 0·1 gram of SiO_2. The silicic acid must not separate in a flocculent condition, but remain in colloidal solution; the titration with permanganate should be made without delay. If the reduction of the iron be effected in another manner and no mercurous chloride be present, the silicic acid alone is capable of inhibiting the oxidation of the hydrochloric acid in the same way as the manganous salt. J. F. B.

The Estimation of Zirconium. PAUL NICOLARDOT and ANTOINE REGLADE (*Compt. rend.*, 1919, **168**, 348—351).—Zirconium is quantitatively precipitated either in neutral solution or in the presence of sulphuric acid, up to 20% of acid, by the addition

of ammonium phosphate, the precipitate being calcined, ignited, and weighed as the pyrophosphate, using the factor 0·487 for converting the weight of pyrophosphate into weight of oxide. This method may be used for the separation of zirconium from iron, chromium, and aluminium. In the presence of iron and chromium an acidity equal to 20% sulphuric acid is necessary to keep up these two metals, but if aluminium is the only other metal present 10% acid is sufficient. W. G.

A Microchemical Reaction for Gold, Silver, and Rubidium (Cæsium). FRIEDRICH EMICH (*Monatsh*, 1918, **39**. 775—776).—Blood-red crystals are formed when solutions of gold chloride are brought into contact with silver chloride and rubidium chloride; these can be employed in the detection of the three metallic ions. The place of rubidium may be taken by cæsium and probably by potassium. The new salts appear to be comparable with the well-known triple nitrites, and, like the latter, promise to be useful in micro-analysis. H. W.

The Estimation of the Methoxyl Group. JOHN THEODORE HEWITT and WILLIAM JACOB JONES (T., 1919, **115**, 193—198).

[**Estimation of Methoxyl Groups.**] M. HÖNIG (*Monatsh.*, 1918, **39**, 871—872).—In a recent communication (Hönig and Spitzer, A., 1918, i, 375), a method of estimating methoxy-groups in substances containing sulphur has been described in which the methyl iodide and hydrogen sulphide are absorbed in pyridine containing silver nitrate, and the estimation is completed after removal of the silver sulphide; the procedure was erroneously designated as a modification of the method of Kirpal and Bühn, who, however, employed pure pyridine only. Further details with respect to the accuracy of the new method are promised in a subsequent communication. H. W.

Estimation of the Geraniol Content of Citronella Oil. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 576—581).—The method for the estimation of geraniol in citronella oil given in Schimmel & Co.'s Bericht (A., 1900, ii, 175; 1912, i, 880) is based on quantitative esterification of the geraniol by phthalic anhydride, and this the author finds to be impossible of attainment, although with mixtures of geraniol and citronellal this method gives results differing but little from the true values; the amount of citronellal esterified by phthalic anhydride increases with that of the geraniol present. Similarly, the esterification of citronellal by means of acetic anhydride is increased by the presence of either acetic acid or geraniol, but complete esterification is here not possible without the use of sodium acetate. T. H. P.

Modifications of Benedict's and Folin's Quantitative Sugar Methods. HOWARD D. HASKINS (*J. Biol. Chem.*, 1919, **37**, 303—304).—In using Benedict's method (compare A., 1911,

ii, 340), sodium thiocyanate may replace potassium thiocyanate in preparing the solution if 105 grams of the former salt are used in place of 125 grams of the latter. In Folin's modification (compare A., 1918, ii, 207) of this method, the author recommends for the mixture of salts 20 grams of sodium thiocyanate, 60 grams of anhydrous sodium carbonate, and 100 grams of disodium hydrogen phosphate, using 4 grams of this mixture for each estimation, and boiling for only half the time recommended by Folin. W. G.

Titration of Sugars by Rupp and Lehmann's Method. E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 180—187).—This method (A., 1909, ii, 442) yields trustworthy results only when carried out under the exact conditions as to concentration of the solutions, etc., employed in constructing the sugar tables used for reference. In the iodometric titration of the excess of copper, an aliquot portion of the solution should be taken if the amount of unreduced copper is large. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Estimation of Soluble Starch in the Presence of Starch and its Hydrolytic Cleavage Products. JAMES CRAIG SMALL (*J. Amer. Chem. Soc.*, 1919, **41**, 107—112).—The method is based on the insolubility of the blue iodine compound of soluble starch in the presence of a half-saturated solution of ammonium sulphate. Three grams of the sample are dissolved by suspending in 200 c.c. of water and heating to the boiling point. The liquid is made up to 250 c.c., and the unconverted starch removed by filtration or centrifuging; 200 c.c. of the filtrate are then treated with 10 c.c. of a 4% solution of iodine in 6% potassium iodide solution, and an equal volume of saturated ammonium sulphate solution is added. The flocculent precipitate is consolidated in the centrifuge, the clear liquid siphoned off through a filter, and the precipitate is washed about five times by shaking with water, adding an equal volume of saturated ammonium sulphate solution, and centrifuging each time. The washing is continued until the brown coloration due to erythrodextrin has been removed. The blue precipitate in the centrifuge bottle, and any minor portion of it which has been collected on the filter, are washed into a flask with a total volume of water not exceeding 300—400 c.c., and dissolved by boiling, after the addition of 5 c.c. of hydrochloric acid, D 1·125; the iodine is driven off, and the starch is completely saccharified by adding a further 20 c.c. of acid and heating in the boiling water-bath for four hours. The dextrose is determined polarimetrically and calculated as starch. This method gives accurate results, even in the presence of large proportions of dextrins. It is to be noted that the violet iodine compound of amylodextrin is also precipitated by ammonium sulphate if an excess of iodine is present; it is dissolved, however, in the course of the washing, after the excess of iodine has been removed. Amylodextrin may therefore be determined by difference, washing by the above method in the one case,

and with the addition of excess of iodine solution to each wash water in the other. J. F. B.

Glycogen Estimation. I. YAMAKAWA (*Tokyo. Igak. Zasshi*, 1917, **31**, 47—68; from *Physiol. Abstr.*, 1919, **3**, 516).—The tissue is heated with potassium hydroxide at 120°, cooled, neutralised with hydrochloric acid, and then hydrolysed with the same acid. The protein is removed by means of colloidal ferric hydroxide and the dextrose estimated. The removal of the protein is essential, as it acts as a protective colloid. The results obtained in this manner are higher than those by previous methods. W. G.

Simple Method for the Determination of the Digestibility of the Cellulosic Part of Vegetable Fibres, especially of Woody Fibres. P. WAENTIG and W. GIERISCH (*Zeitsch. physiol. Chem.*, 1918, **103**, 87—103).—Recent research on woody matter has shown that thorough removal of the lignified substance from the fibres is necessary in order to obtain material of a moderately high degree of digestibility. The authors have devised a simple method for obtaining rapidly an approximate measure of the non-saccharifiable, and therefore undigestible, material, which interferes with the digestion of the nutrient constituents in woody substances. This method is based on the fact that, when chlorine acts on woody fibre, the lignin is at first almost exclusively attacked, the proportion of lignin present corresponding with that of the chlorine absorbed. By "chlorine number" is understood the percentage increase in weight, calculated on dry matter, occurring when the woody material is subjected under certain definite conditions to the action of a current of moist chlorine. As a general rule, the chlorine number and indigestibility increase or diminish together. [See *J. Soc. Chem. Ind.*, 1919, 195A.] T. H. P.

The Test for Tartrates Depending on the Formation of the Copper Tartrate Complex. L. J. CURTMAN and B. R. HARRIS (*J. Amer. Chem. Soc.*, 1919, **41**, 207).—The statement made by Curtman, Lewis, and Harris (A., 1918, ii, 87) that comparatively small amounts of phosphates or borates, when treated according to Böttger's procedure ("The Principles of Qualitative Analysis," 1906, 159), respond in the same way as tartrates, is now found to be incorrect; neither of these anions, even in amounts as high as 0·5 gram, gives a blue filtrate. T. H. P.

Fat Extraction Apparatus. E. GRIFFITHS-JONES (*Analyst*, 1919, **44**, 45—47).—An extraction flask is attached in the ordinary way by means of a cork to the lower end of a vertical condenser. The material to be extracted is packed into an extraction thimble which is fitted on to the lower end of the condenser tube, the thimble being thus inside the neck of the flask. The vapours of the solvent contained in the flask are conducted through a side-tube which passes just through the cork closing the flask,

and extends upwards and parallel with the condenser to the top of the latter, and then passes down the condenser tube to approximately the level of the water-intake. The condensed solvent falls into the thimble and passes back again into the flask. [See, further, *J. Soc. Chem. Ind.*, 1919, 201A.] W. P. S.

Estimation of "Saccharin" in Tablets. A. Bonis (*Ann. Falsif.*, 1918, **11**, 369—372).—Free sodium hydrogen carbonate is estimated in the tablets by titration with $N/10$-sulphuric acid, using methyl-orange as indicator. The quantity of "saccharin" is found by fusing a portion of the sample with a mixture of sodium carbonate and sodium nitrate, and estimating the sulphate formed; the amount of barium sulphate obtained is calculated into sodium "saccharinate." Free "saccharin" may be present, and is estimated by extraction with ether; in this case, the sodium "saccharinate" remains insoluble, and its quantity may be determined by the fusion method mentioned. Lactose, if present, is estimated separately. *p*-Sulphaminobenzoic acid is detected in the tablets by hydrolysing the sample with hydrochloric acid, concentrating the solution to a small volume, and placing it aside for twenty-four hours; the para-acid crystallises out, and may be collected and weighed. [See, further, *J. Soc. Chem. Ind.*, 1919, 198A.] W. P. S.

Analysis of Commercial "Saccharin." II. Detection and Estimation of Impurities. H. Droop Richmond and Charles Alfred Hill (*J. Soc. Chem. Ind.*, 1919, **38**, 8—10T. Compare A., 1918, ii, 339, and Procter, T., 1905, **87**, 242).—The methods described deal with the following impurities and properties: *Moisture. Mineral matter.* p-*Sulphonaminobenzoic acid.*—1·5 Grams of "saccharin" are heated with 10 c.c. of 70·5% sulphuric acid so that the liquid boils in as nearly as possible one minute, and then boiled for exactly thirty seconds, the solution being then poured at once into 15 c.c. of distilled water kept cool by immersion of the vessel in cold water; after mixing, the solution is cooled under the tap, seeded with a trace of the para-acid, and placed in ice-water. If present to the extent of 1%, para-acid crystallises out in thirty minutes or less; if 3% is present, the crystals usually begin to separate before seeding on cooling, and when about 10% is present, the acid begins to crystallise in the hot. o-*Sulphonaminobenzoic acid.* o-*Toluenesulphonamide.*—This dissolves in sodium hydrogen carbonate, whilst "saccharin" is insoluble. *Lead. Arsenic. Ammonia. Easily carbonisable organic matter.*—The test of the British, French, and U.S. Pharmacopœias may be replaced by the coloration obtained in the test for para-acid with 70·5% sulphuric acid (see above). *Sweetness. Melting point.*—Pure "saccharin" has m. p. 229°. *French Codex identification test.*—When heated in a test-tube with a small crystal of resorcinol and several drops of concentrated sulphuric acid, "saccharin" gives a liquid at first reddish-yellow and then dark green. Treatment of the cooled liquid with water and supersaturation with

sodium hydroxide gives a liquid showing intense green fluorescence. This test is, however, not characteristic of "saccharin," since the ortho-acid gives the same result, and the amide a moderate fluorescence. T. H. P.

Microchemical Identification of Stovaine and Cocaine. Denigès (*Bull. Soc. Pharm., Bordeaux*, 1917; from *Ann. Chim. anal.*, 1919, [ii], **1**, 65—66).—The tests described are carried out on a microscope slide, a small drop of the solution being treated with a drop of the reagent. Platinum chloride does not give a precipitate with a 0·5% stovaine hydrochloride solution, but a fine, granular precipitate is obtained with a 1% solution; in the case of cocaine hydrochloride solution of either of the above concentrations, a characteristic, crystalline precipitate is formed. Gold chloride gives a crystalline precipitate with both alkaloids, but the form of the crystals is quite different for the two salts. Picric acid yields a yellow, crystalline precipitate with stovaine hydrochloride, whilst cocaine picrate is amorphous and changes to yellow, liquid droplets when stirred. [See, further, *J. Soc. Chem. Ind.*, 1919, 198A.] W. P. S.

Estimation of Morphine in Complex Products. III. Opium and Mixtures containing Opium. Alfred Tingle (*Amer. J. Pharm.*, 1918, **90**, 851—861. Compare this vol., ii, 87, 88).—The presence of resinous matters in opium interferes with the estimation of morphine by the methods described previously (*loc. cit.*); the greater part of these resins may be separated by heating the slightly alkaline solution containing them, together with the morphine, with an excess of salicylic acid. When the mixture is cooled, the resin is precipitated, and may be removed by filtration. The morphine is then precipitated from the filtrate, collected, redissolved, extracted with alcohol-chloroform mixture, and titrated. [See, further, *J. Soc. Chem. Ind.*, 1919, 116A.] W. P. S.

New Titration Method for the Determination of Uric Acid in Urine. J. Lucien Morris (*J. Biol. Chem.*, 1919, **37**, 231—238).—A slight modification of the method described for the estimation of uric acid in blood (compare A., 1918, ii, 251). W. G.

[Detection of Traces of Blood Pigment.] John Alexander Milroy (*Biochem. J.*, 1918, **12**, 327—329).—See this vol., i, 179.

Impurity in Ethyl Ether giving a Blue Coloration with Benzidine. F. Weehuizen (*Pharm. Weekblad*, 1919, **56**, 301—303.)—Attention is directed to the presence in some samples of ethyl ether used for analytical purposes of an impurity which gives a blue coloration on addition of hydrogen peroxide and benzidine. Pieces of potassium hydroxide kept in the ether for a time are sufficient to remove the impurity. W. S. M.

The Value of Walker's Method of Estimating Casein in Milk. A. AGRESTINI (*Staz. sper. agr. Ital.*, 1917, **50**, 109—114; from *Chem. Zentr.*, 1918, ii, 866).—Comparisons of the rapid method devised by Walker (A., 1914, ii, 309) with the process of Schlossmann and von Bondzinski show the former to be very convenient, but not completely trustworthy. The amounts of alkali required to produce neutrality in Walker's procedure after addition of formalin are either identical with or very near to those required in the direct titration of the original milk. This result appears to support the view of Bordas and Touplain (A., 1911, ii, 631) that the acidity of fresh milk depends mainly on the casein, and allows an approximate estimation of the latter by simple titration in the presence of phenolphthalein as indicator. H. W.

Vernes' Method (Sero-diagnosis of Syphilis). ROGER DOURIS and ROBERT BRICQ (*Bull. Soc. chim.*, 1918, [iv], **23**, 472—478. Compare Vernes, *Compt. rend.*, 1917, **165**, 769; 1918, **166**, 575; **167**, 383).—Vernes has shown that serum in the presence of an inorganic or organic colloidal suspension causes a periodic precipitation, the rhythm of which differs according as the serum is normal or syphilitic, and that it is possible to prepare a fine organic suspension of a determined stability which will flocculate with a certain dose of syphilitic serum, but not with the same dose of normal serum. The authors give full details for carrying out the test, using red globules from sheep's blood, pig serum, and "perethynol" (an absolute alcoholic extract of dried, powdered, and de-fatted horse-heart muscle), and measuring, not the flocculation, but the hæmolysis colorimetrically. W. G.

Estimation of Acidity and Titratable Nitrogen in Wheat with the Hydrogen Electrode. C. O. SWANSON and E. L. TAGUE (*J. Agric. Res.*, 1919, **16**, 1—15).—Aqueous extracts of wheat were made at 5°, 20°, 40°, and 50°, the mixture being shaken for times varying from five minutes to twenty-four hours. The hydrogen-ion concentration of the extract as measured by the hydrogen electrode is practically independent of the temperature and the duration of the extraction, but the volume of $N/20$-barium hydroxide solution necessary to add to bring the extract to a definite P_H value increases with the time of shaking, and within certain limits is proportional to it. As the duration increases, the volume of standard alkali required increases up to a limit, which is reached sooner as the temperature of extraction rises. This phenomenon is due to the presence in the extract of substances which only become ionised when an alkali is added.

The amino-nitrogen, as determined by Sörensen's formaldehyde method, is all extracted in two hours at 40°. The amount of phosphorus in the extract made at 20° directly precipitable by magnesia mixture is about one-half of the total phosphorus present, but at 40° practically the whole of the phosphorus is converted into a form which is precipitated by magnesia mixture. W. G.